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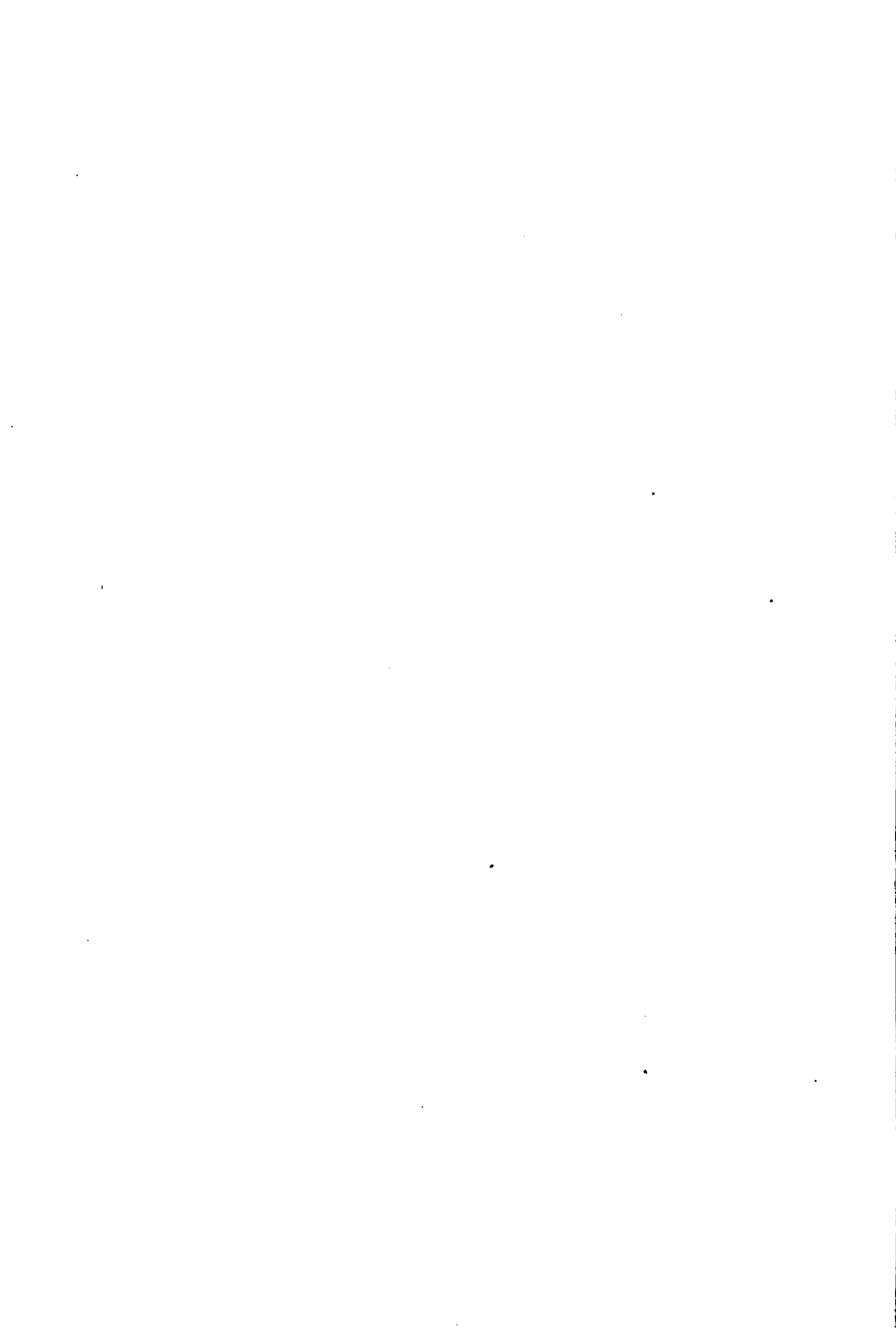
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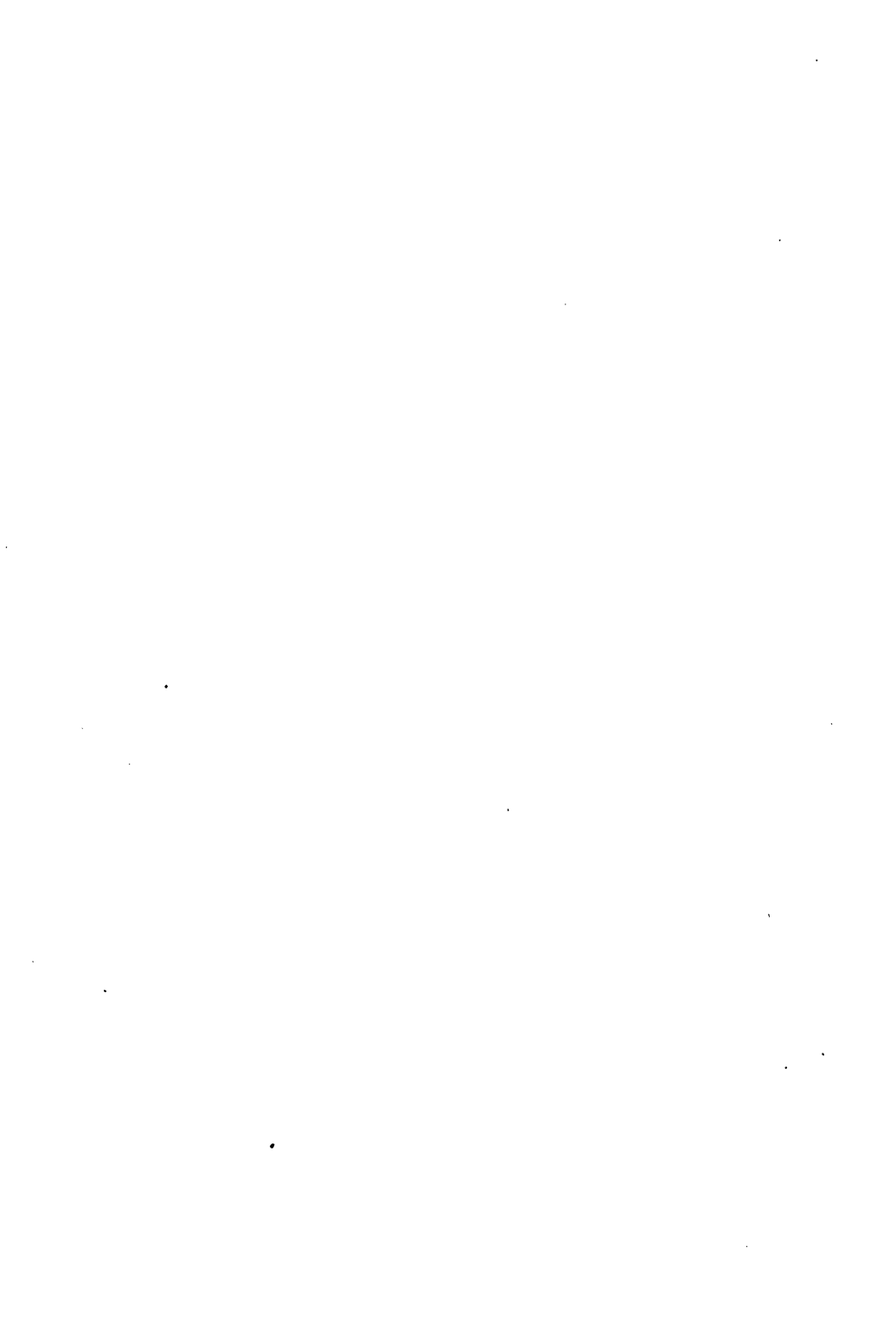


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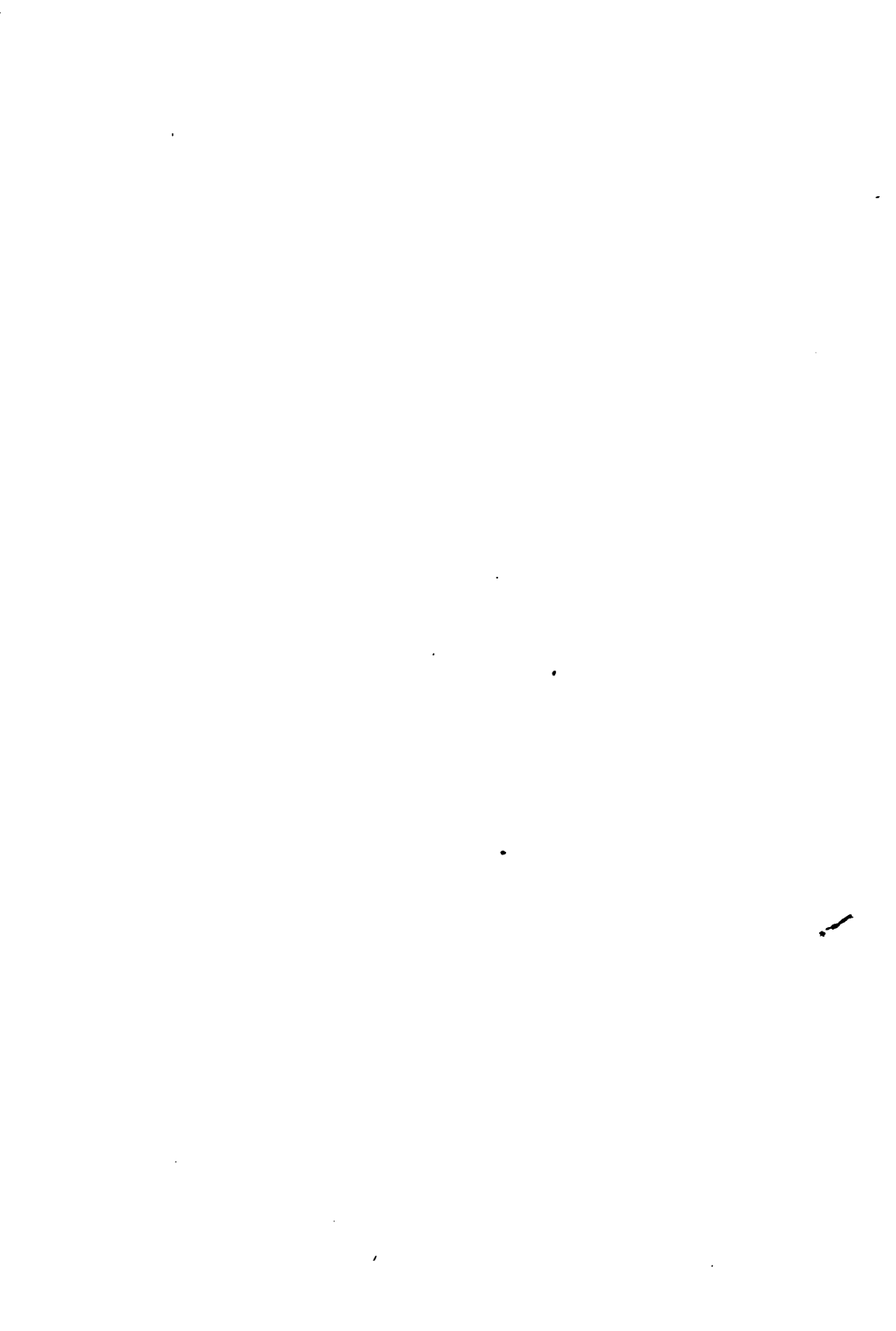


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LABORATORY MANUAL
OF
QUALITATIVE ANALYSIS



LABORATORY MANUAL
OF
QUALITATIVE ANALYSIS

BY
WILHELM SEGERBLOM, A.B.
INSTRUCTOR IN CHEMISTRY AT THE PHILLIPS EXETER
ACADEMY

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PREFACE

THE large number of books on Qualitative Analysis already published shows that the ideal presentation of the subject has not yet been attained. Because of so much legitimate variation and choice within the ranks of possible methods, perhaps it is unlikely that any one book will be satisfactory to the majority of analytical teachers. This little book does not presume to be "the one"; it is simply a statement of the method that has worked well with the classes at The Phillips Exeter Academy. I believe that texts for beginners in Qualitative Analysis should be arranged so that the work increases in severity as the analytical powers of the student are developed, and chemical analysis adapts itself admirably to this purpose, particularly if the groups of bases are studied in the order presented by Fresenius and still followed by some of the best writers on the subject.

All the preliminary work given in these pages should be done by the instructor on the lecture desk. The results are printed in full so as to enable the student to devote his whole attention to the phenomena and to the instructor's remarks thereon. A repetition of the experiments by the students individually in the laboratory will clinch this most important foundational work and pave the way for a comprehensive grasp of the methods of separation in the case of unknown substances. Only those reactions that lead to such a grasp are given; all others, however interesting, are rigorously excluded. A known solution on each group of bases containing all the members thereof should be analyzed by the instructor in the presence of the class; each student should repeat this work before proceeding with his own unknown solutions.

I believe heartily in the "scheme" or "outline" method of presenting the best processes of analysis, for it gives the student at a glance some idea of the relative importance of the different parts of the procedure; he sees, too, much more easily than if it were all hidden in monotonous pages of ordinary text matter, not only the skeleton framework upon which the different steps of the analysis are supported, but also the thread of logical separation and elimination that runs through the entire basic analysis.

If the student follows the schemes mechanically, as some aver he is likely to, it is the fault more of the teacher than of the scheme; for nothing except judicious and frequent questioning by the teacher will keep the ordinary student from following mechanically any text on Qualitative Analysis; and this questioning is of double value if it comes at the working desk and leads the student to think his own way out of his difficulties. The proper mental attitude is not so much, "What do I do next?", as "What was the reason for that last step?" and "What substances have I here now?"

The schemes contain full and sufficient directions for ordinary analyses. The notes are intended to answer such questions as arise in the alert mind and to point out hidden snags and how to avoid them. The little degree marks ($^{\circ}$) in the text of the schemes are made inconspicuous purposely, so as not to interfere with the first reading, but to call the attention, upon the second reading, when perhaps the solution does not go right, to the fact that "there is a note on that" which will throw additional light on the troublesome step.

The lists of equations are made complete so that the student shall not be disappointed when he looks up the equations for any doubtful reactions.

It is needless to say that this little book is not designed for first-year work. It can be taken up more profitably by students who have already been introduced to the methods of the laboratory in a previous course in elementary chemistry. A

course of lectures in descriptive chemistry accompany it to advantage.

For the ruling and arrangement of the Table of Solubilities I am responsible; as given here it is a reprint of a larger copyrighted Table of Solubilities published separately some time ago.

Although many works on Qualitative Analysis have been examined in the preparation of this little book for the press, credit should be given for those that have been found most helpful, namely, those of Fresenius, Treadwell, Prescott and Johnson, Hill, and A. A. Noyes. From these, of course, were gleaned the facts; for the arrangement I assume the responsibility myself. Thanks are gratefully accorded those of my pupils and other friends who by criticism or suggestion have aided in perfecting these pages. The assistance of Mr. Augustus Klock, High School, Beverly, Mass., and of Dr. L. D. Bissell, St. Paul's School, Concord, N.H., in reading the proof is gladly acknowledged. Any corrections or comments will be gratefully received.

W. S.

EXETER, N.H., 1907.

CONTENTS

(References are to sections.)

PART I

INTRODUCTION

QUALITATIVE ANALYSIS	1
ROBERT BOYLE	2
REQUIREMENTS	3
TERMS	5
BERTHOLLET'S LAWS	6
REAGENTS	7
APPARATUS	10
COURSE OF STUDY	12
ABBREVIATIONS	13

PART II

BASIC ANALYSIS

LIST OF BASES BY GROUPS	14
GROUP I	
List of Members	24
Flame Tests	25
Test for NH_4	26
Scheme for Group I	27
Notes on Scheme for Group I	28
GROUP II	
List of Members	35
Preliminary Work	36
Table of Preliminary Work	38
Equations for Preliminary Work	39

(References are to sections.)

Scheme for Group II	47
Notes on Scheme for Group II	48
Equations for Scheme for Group II.	63
Laboratory Notes on Unknown Solutions	71
Sample Page from Laboratory Note-book	72
Scheme for Separation of Groups I and II	74
Notes on Scheme for Groups I and II	75

GROUPS III AND IV

List of Members	80
Preliminary Work	81
Table of Preliminary Work	82
Ferrous and Ferric Iron	83
Equations for Preliminary Work	90
Scheme for Groups III and IV	100
Notes on Scheme for Groups III and IV.	103
Equations for Scheme for Groups III and IV.	141
Scheme for Separation of Groups I, II, III, and IV	166
Notes on Scheme for Groups I, II, III, and IV	167

GROUP V

List of Members	170
Preliminary Work	171
Table of Preliminary Work	172
Equations for Preliminary Work	173
Scheme for Group V	179
Notes on Scheme for Group V	180
Equations for Scheme for Group V.	205
Scheme for Separation of Groups I, II, III, IV, and V	219
Notes on Scheme for Groups I, II, III, IV, and V	220

GROUP VI

List of Members	227
Preliminary Work	228
Table of Preliminary Work	229
Equations for Preliminary Work	230
Scheme for Group VI	238
Notes on Scheme for Group VI	239
Equations for Scheme for Group VI	254

CONTENTS

xi

(References are to sections.)

Scheme for Separation of Groups I, II, III, IV, V, and VI . . .	260
Notes on Scheme for Groups I, II, III, IV, V, and VI . . .	261
PRESENCE OF PHOSPHATES AND OXALATES IN GROUPS III AND IV	272

PART III

ACID ANALYSIS

LIST OF ACIDS BY GROUPS	288
PRELIMINARY WORK	292
TABLE OF PRELIMINARY WORK ON ACIDS	296
EQUATIONS FOR PRELIMINARY WORK	297
SPECIAL TESTS FOR ACIDS	301
SCHEME FOR ACID ANALYSIS	327

PART IV

SALT ANALYSIS

INTRODUCTION	331
PRELIMINARY ANALYSIS	
General Properties	334
Heating in Bulb Tube	335
Heating on Charcoal Alone	336
Heating on Charcoal with Na_2CO_3	337
Borax Bead	338
Flame Coloration	339
Action with Concentrated H_2SO_4	340
Notes on Scheme for Preliminary Analysis of Salts	341
PREPARATION OF THE SOLUTION	348
TREATMENT WITH WATER	349
TREATMENT WITH ACIDS	354
ACID ANALYSIS	365
TABLE OF SOLUBILITIES	372
TREATMENT OF SUBSTANCES INSOLUBLE IN WATER AND ACIDS	373
BOILING WITH SODIUM HYDRATE	376

(References are to sections.)

SPECIAL TESTS BEFORE FUSION	377
FUSION WITH SODIUM CARBONATE	381
FUSION WITH ACID POTASSIUM SULPHATE	387
SAMPLE PAGE FROM LABORATORY NOTE-BOOK	390

PART V

APPENDIX

COLLATERAL READING	391
DIVISION OF WORK IN QUALITATIVE ANALYSIS	392
STUDY QUESTIONS	394
COMPLETE LIST OF REAGENTS	
Individual Reagents	408
General Reagents	409
Reagents to be used in Preliminary Work for Bases and for making up Unknown Solutions	410
Reagents to be used in Preliminary Work for Acids	421
SUGGESTIONS TO THE TEACHER	422

INDEX	PAGE 129
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PART I

INTRODUCTION

1. **Qualitative Analysis** is that branch of Chemistry which treats of the recognition of elements or their compounds. It presupposes considerable acquaintance on the part of the student with the preparation and behavior of the more common elements and compounds, gained preferably through laboratory work.

2. **Robert Boyle** (1626–1691) is often called “The Father of Qualitative Analysis” because he was the first to apply the term *analysis* to the use of certain plant juices like litmus in testing for acids and alkalies; and he recognized the presence of certain metals, not by isolating them, but by causing a precipitate characteristic of that metal to come down through the addition of a second substance. Many of Boyle’s original tests are at the basis of the modern schemes of analysis.

3. **Four requirements** are essential for successful work in Qualitative Analysis. They are :

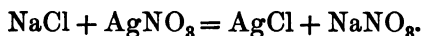
(1) A considerable knowledge of the properties and chemical behavior of elementary substances and their more important compounds ;

(2) A keen and accurate observation of phenomena presented by experiments ;

(3) The power to draw the right conclusions from the observations made ;

(4) A knowledge of the conditions under which a certain phenomenon is conclusive proof of the presence of a certain element.

4. It is assumed that the first three have been acquired in the first year's work in Chemistry. The last may be illustrated by an example. If a solution of sodium chloride be added to a silver nitrate solution, the familiar precipitate of silver chloride comes down, the reaction being represented by the following equation :



It is well known that silver chloride is insoluble in water, and the presence of the sodium nitrate in the resulting liquid does not seem to affect the solubility of the precipitate. If the silver chloride be separated from the solution and divided into two parts, and one part treated with dilute nitric acid and the other with ammonium hydrate, it is found that the first part does not dissolve, while the second part does dissolve. It is fair to assume, then, that if nitric acid is present with the silver nitrate when the sodium chloride is added, the precipitation of the silver chloride is not obstructed ; but if ammonium hydrate is present with the silver nitrate when the sodium chloride is added, the expected precipitate of silver chloride will not come down, though silver is present in the solution. This may easily be verified by experiment, and shows the importance of keeping track of everything that may be present in a solution under examination.

5. The following terms are used frequently in Qualitative Analysis. A *reaction* is any phenomenon exhibited by a substance ; it is said to take place *in the wet way* if the substances used are in solution, as in the experiment with silver nitrate mentioned above ; it is said to take place *in the dry way* if no water is present, as in getting oxygen from red oxide of mercury or in testing the flame coloration of dry salts. A *reagent* is any known substance used in effecting a reaction, as sodium chloride or ammonium hydrate in the experiment above. A *general reagent* precipitates several substances, and the mixed precipitate requires further testing to identify the separate sub-

stances. A *special reagent* is used in testing for a single substance. A *precipitate* is an insoluble substance separating when two solutions are mixed; if it settles readily, it may be separated from the liquid by *decantation*, — pouring off the clear liquid, which is then called the *decantate*, — or by *filtration* through a filter paper, when the resulting liquid is called the *filtrate*. The general methods and the apparatus used in such processes as precipitation and filtration are not illustrated here because it is assumed that the student has learned about them in his elementary work. Special methods for particular cases will be given in the body of the text, as occasion arises.

6. Many of the more important reactions of Qualitative Analysis run according to **Berthollet's Laws**, which may be stated as follows: *When two factors can form a product that is insoluble or volatile under the conditions of the reaction, that insoluble or volatile product will be formed till one of the factors is used up.* This is well illustrated by the precipitation of silver chloride, or by the evolution of carbon dioxide from a carbonate by the action of hydrochloric acid.

7. **Reagents.** — Each student should be supplied with a set of liquid reagents kept in 500 c.c. glass-stoppered bottles with blown labels. It is most convenient to have them arranged upon two shelves one over the other and in the following order reading from left to right on the shelf:

UPPER SHELF

H_2SO_4 Dil	dilute sulphuric acid
HNO_3 Dil	dilute nitric acid
HCl Dil	dilute hydrochloric acid
$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	plumbic acetate
NH_4Cl	ammonium chloride
NH_4OH	ammonium hydrate
$(\text{NH}_4)_2\text{CO}_3$	ammonium carbonate
$(\text{NH}_4)_2\text{C}_2\text{O}_4$	ammonium oxalate
$(\text{NH}_4)_2\text{S}$	ammonium sulphide
AgNO_3	silver nitrate

LOWER SHELF

H_2SO_4 Conc	concentrated sulphuric acid
HNO_3 Conc	concentrated nitric acid
HCl Conc	concentrated hydrochloric acid
$\text{HC}_2\text{H}_3\text{O}_2$	acetic acid
BaCl_2	barium chloride
CaCl_2	calcium chloride
CaSO_4	calcium sulphate
NaOH	sodium hydrate
Na_2HPO_4	sodium phosphate

8. It is well to keep the bottles always in this order and after using a reagent to return the bottle immediately to its place on the shelf. This inculcates orderliness, neatness, and saving of time. The stoppers should never be interchanged or laid upon the desk; contamination of reagents may be avoided by removing the stopper with two fingers of the hand that holds the bottle. It is well to remember that in Qualitative Analysis orderliness and cleanliness lead to perfection and correct results.

9. The reagents mentioned above should be supplied to each student when he begins his laboratory work. A complete list of all the reagents needed for the work indicated in this book is given in section 407.

10. **Apparatus.** — Each student should be supplied with the following articles :

Laboratory notebook.	Three 150 c.c. prescription bottles.
Ring stand.	
Large ring.	Two 250 c.c. flasks.
Medium ring.	Two 500 c.c. flasks.
Small ring.	Two nests of 3 beakers each.
Tripod.	Two 10 cm. funnels.
Bunsen burner and hose.	Two 7.5 cm. funnels.
Bat-wing burner and hose.	Two 5 cm. watch glasses.
Blast burner.	One 50 c.c. graduate.

Twenty-four large test tubes.	Triangular file.
Six salt tubes.	One pair steel forceps.
One meter glass rod.	One mouth blowpipe and hose.
Two meters glass tubing.	Two platinum test wires.
Two porcelain evaporating dishes, 11 cm. diameter.	Platinum foil, 3 cm. square.
One 250 c.c. porcelain casserole.	One thick cobalt glass.
Porcelain mortar and pestle.	One box filters, 20 cm. diameter.
Porcelain crucible.	One box filters, 12.5 cm. diameter.
Crucible tongs.	One box of labels.
Filter arm.	Six rubber connectors.
Test tube rack.	Two 2-hole rubber stoppers for the 500 c.c. flasks.
Test tube brush.	Six corks.
Two fine iron gauzes.	Two towels.
Two coarse iron gauzes.	Sponge.
Two asbestos sheets.	

11. Each student should make two wash bottles, one for cold water and the other for hot; the neck of the latter should be wound with stout string to protect the hand from the heat. He should also make up stirring rods with fire-polished ends for the different beakers; a few of these rods should have a crook at one end so that they can be hung on a ring of the ring stand when not in use. The most convenient notebook to use is one having about two hundred pages of unruled paper, with pages seventeen by twenty-one centimeters in size. The book should be strengthened with leather back and corners, because laboratory usage is apt to destroy the light cloth back of the ordinary pasteboard-covered blank book.

12. **Course of Study.** — The work laid out in this book is divided into three parts. The analysis of unknown solutions for the metals or *bases* will be taken up first; this will be followed by the special tests for *acids* or acid radicals; the combination of these two in the examination of *salts* will complete the course.

13. Abbreviations.—The following abbreviations and signs are used in these pages :

F.	filtrate.
P.	precipitate (in the schemes).
ppt.	precipitate (in the preliminary work).
ppts.	precipitates.
pptd.	precipitated.
reppts.	reprecipitates.
repptd.	reprecipitated.
R.	residue.
immed.	immediate.
Gr.	group.
pres.	present.
abs.	absent.
sl.	slightly.
sol.	soluble.
soln.	solution.
insol.	insoluble.
decomp.	decomposed.
dil.	dilute.
conc.	concentrated.
cm.	centimeter.
c.c.	cubic centimeter.
∴	therefore.
Aq	water of solution or of dilution.
Bx. Bd.	borax bead.
Gen. Prop.	general properties.
B. T.	bulb tube.
Ch.	charcoal.
Fl.	flame.
Prelim.	preliminary.

PART II

BASIC ANALYSIS

LIST OF BASES BY GROUPS

14. Only the more common metals, or bases as they are sometimes called, will be tested for in the study of unknown substances; they fall naturally into the six following groups, each group having certain characteristics which distinguish it from the other groups. The tests for gold, platinum, uranium, and other rare metals are outside the scope of this book, and for such tests the student is referred to any of the larger works on Qualitative Analysis.

15. GROUP I. *Alkali Group.*

Na	Sodium.	Sulphides and carbonates are soluble in water.
K	Potassium.	
Li	Lithium.	
NH ₄	Ammonium.	

16. GROUP II. *Alkaline-earth Group.*

Ba	Barium.	Sulphides are soluble in water, sometimes with decom- position; carbonates are in- soluble in water.
Sr	Strontium.	
Ca	Calcium.	
Mg	Magnesium.	

17. GROUP III. *Aluminium Group.*

Al	Aluminium.	Sulphides are not formed in the wet way. (NH ₄) ₂ S pre- cipitates the hydrates.
Cr	Chromium.	

18. GROUP IV. *Iron Group.*

Fe	Iron.	Sulphides are precipitated
Co	Cobalt.	by $(\text{NH}_4)_2\text{S}$ in alkaline solu-
Ni	Nickel.	tion but not in acid solution.
Mn	Manganese.	
Zn	Zinc.	

19. GROUP V. *Copper Group.*

Ag	Silver.	Sulphides are precipitated
Pb	Lead.	by H_2S in acid solution, and
Hg	Mercury.	are insoluble in $(\text{NH}_4)_2\text{S}_2$.
Cu	Copper.	
Cd	Cadmium.	
Bi	Bismuth.	

20. GROUP VI. *Tin Group.*

As	Arsenic.	Sulphides are precipitated
Sb	Antimony.	by H_2S in acid solution, but
Sn	Tin.	are soluble in $(\text{NH}_4)_2\text{S}_2$.

21. In the ordinary examination of an unknown solution for bases it is necessary to separate the groups from each other before testing for the individual members of each group. This separation is effected by adding the group reagents in the proper order so that each precipitates one group only, leaving in solution such members of all other groups as may be present. Each group-precipitate is then examined by itself for the individual members that may be present.

22. In these pages, however, the groups will be studied separately in the order given above. The reasons for this will appear later. The mode of study will be as follows: The action of the more common reagents with solutions of the separate members of the group will be taken up first; this constitutes the Preliminary Work, and it will be followed by the complete analysis according to the Scheme of a known solution containing all the members of the group. The analysis of three un-

known solutions containing several members of the group will show if the preceding work has been done intelligently. Before the next group is taken up, the combination of the group in question with the preceding groups will be considered. Then the next group will be taken up, first alone, and then in combination with the preceding groups.

23. It is customary to say that we “test for Na” or we “test for Ag”; in very few cases is it necessary or advisable to isolate the elements as such; it is much more convenient to show the presence of a certain metal by producing, with the proper reagent, a compound or a reaction that is characteristic of the metal under consideration and that differentiates it from all other metals under like conditions. Good examples are the yellow flame coloration of sodium compounds, and the white, curdy precipitate produced when silver nitrate is added to a solution containing a chloride.

GROUP I. Na, K, Li, NH₄

24. List of Members. — The members of Group I are :

Na	Sodium.
K	Potassium.
Li	Lithium.
NH ₄	Ammonium.

The first three members are often called the alkali metals on account of the strongly alkaline character of their hydrates. The radical, NH₄, though strictly not a metal, is usually included in Group I on account of the similarity between its compounds and those of the alkali metals. The first three members of this group are recognized by the color imparted to the Bunsen flame by any of their compounds. The last one is recognized by a special test.

25. Flame Tests. — Clean a platinum test wire by holding it in the colorless Bunsen flame until it no longer imparts any color to the flame. The wire will, of course, become red-hot; the flame, however, is the part to be examined, and it should

have the same color, or lack of color rather, above the wire as below it. If simply heating the wire does not clean it, occasional dipping in dilute hydrochloric acid and reheating will help. Then pick up a crystal of potassium chlorate, KClO_3 , with the red-hot platinum wire and hold it in the colorless Bunsen flame. Note the color of the flame; then repeat, examining the color of the flame by looking at it through a cobalt glass, — a plate of glass of deep blue color which has the power of allowing the rays from the potassium only to pass through. The colorless Bunsen flame may be seen through the cobalt glass, but this may be disregarded, as it is not a distinct color. When the wire is clean and imparts no more color to the flame, repeat the above tests, using lithium chloride, LiCl , alone, and then using sodium carbonate, Na_2CO_3 , alone. If the blue of the cobalt glass is deep enough, the sodium flame will not be visible through the glass; if it is not deep enough, the sodium flame may be visible; in the latter case use several pieces of cobalt glass. Finally try the flame given by a mixture of K and Na salts and then of a mixture of Li and Na salts. Verify the following results :

KClO_3 gives violet to naked eye, pink through cobalt glass.

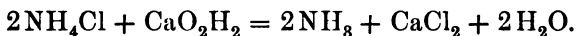
LiCl gives red to naked eye, nothing through cobalt glass.

Na_2CO_3 gives yellow to naked eye, nothing through cobalt glass.

$\text{KClO}_3 + \text{Na}_2\text{CO}_3$ gives yellow to naked eye, pink through cobalt glass.

$\text{LiCl} + \text{Na}_2\text{CO}_3$ gives yellow then red to naked eye, nothing through cobalt glass.

26. Test for NH_4 . — Mix in a test tube equal portions of dry CaO_2H_2 and a dry NH_4 salt, NH_4Cl for instance, add enough water to make a paste, and place upon the mouth of the test tube the convex side of a watch glass with a piece of turmeric paper stuck on the under side by wetting it with water. The reaction that takes place in the test tube is represented by the equation:



If the turmeric paper does not change color, heat the test tube gently to drive off the NH_3 . Care must be taken not to have any CaO_2H_2 at the top of the test tube, for that of course will discolor the test paper where it touches the test tube; the brown color due to the NH_3 should be densest at the center.

27. Scheme for Group I.—Take 10 c.c. of a solution containing all four members of Group I and evaporate to dryness. Test the residue by flame for Na, K, and Li as in section 25. In a little of the original solution test for NH_4 as in section 26.

28. Notes on Scheme for Group I.—The following notes will be found of service in throwing further light on the analysis of a solution for the members of Group I.

29. Na is always apparent by the flame test to the naked eye when this metal is present. It will often be found present in small quantities, even in so-called chemically pure salts. If the yellow burns off in about a quarter of a minute, it is safer to report only a trace of Na present.

30. The flame test for Na is extremely delicate, so delicate, in fact, that a millionth part of a milligram of sodium may be recognized by means of the spectroscope. Practically, sodium occurs so frequently and is so persistent that simply rubbing a clean test wire with the fingers once will transfer enough sodium compounds to the wire to give a distinct yellow flame coloration. The spectroscope consists of a glass prism and two tubes. A slit in the end of one tube allows a ray of light to fall upon the prism, which refracts the ray and breaks it up into the spectrum colors; the refracted ray passes into the other tube, containing a telescope, where the colored lines characteristic of the different elements may be seen in magnified form.

31. Li will sometimes be obscured if much Na is present, but it will usually flash out intermittently.

32. The K flame as seen through the cobalt glass is characteristic, and is different from the flame that much Na will sometimes give through the cobalt glass when the glass is too thin. In case of doubt about the test for K, try a little KClO_3 on a clean wire and compare the flame of this with the flame of the unknown substance. This is called a "blank test."

33. The following **wet test for K** may be employed if the flame test is unsatisfactory: Evaporate the solution supposed to contain K to dryness and then ignite gently till all the white fumes of NH_4 salts are gone. Dissolve in as little water as possible, filter if necessary, add a few drops of hydrochloroplatinic acid, H_2PtCl_6 , shake, and let stand awhile. A yellow precipitate of potassium chlorplatinate, K_2PtCl_6 , indicates the presence of K. H_2PtCl_6 produces no precipitate in Na and Li solutions; in K and NH_4 solutions it produces yellow precipitates that are slightly soluble in water; hence the necessity of expelling the NH_4 salts entirely, and of having the solution concentrated.

34. When the test wire is not in use it is well to make an S-bend in it close to the handle and hang it by this bend on the top of the Bunsen burner so that any salt that may be on the wire will burn off while you are busy with other parts of the analysis.

GROUP II. Ba, Sr, Ca, Mg

35. List of Members.—The members of Group II are:

Ba	Barium.
Sr	Strontium.
Ca	Calcium.
Mg	Magnesium.

The first three members are often called the alkaline-earth metals because of the somewhat alkaline character of their hydrates. Magnesium is usually included in Group II because its compounds resemble those of the alkaline-earth metals more closely than those of any other metals. Although the members of Group II give fairly good flame tests, it is considered better to test for their presence or absence in the wet way.

36. Preliminary Work.—In four test tubes put equal amounts of solutions of BaCl_2 , SrCl_2 , CaCl_2 , and MgSO_4 . To each add a little $(\text{NH}_4)_2\text{CO}_3 + \text{Aq.}$ Note the colors and relative amounts of the precipitates formed; examine each precipitate closely to see if it is gelatinous, finely divided, or granular, and if it settles well. Shake the test tube containing Ba a little, and when the precipitate is well mixed with the liquid pour off half the

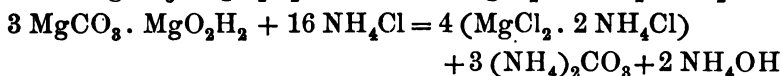
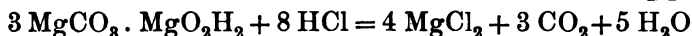
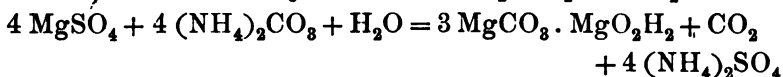
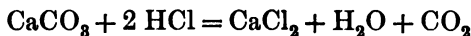
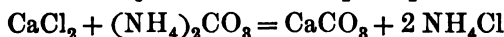
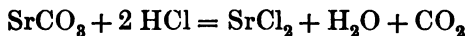
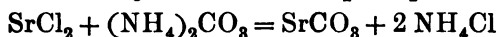
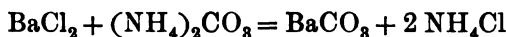
emulsion into another test tube. To one half add $\text{NH}_4\text{Cl} + \text{Aq}$ and to the other dilute HCl , and see if these reagents dissolve the BaCO_3 . Repeat these experiments with the other members of the group. In a similar manner add to fresh portions of the solutions of the four members of this group small portions of NH_4OH , dilute H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4 + \text{Aq}$, $\text{K}_2\text{CrO}_4 + \text{Aq}$, $(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{Aq}$, and $\text{Na}_2\text{HPO}_4 + \text{Aq}$. Note carefully all the precipitates formed and verify all the results in the table in section 38. A word of explanation as to tables and their use may not be out of place here. Roughly speaking, the tables fall into two classes—first, those dealing with the preliminary work for the different groups of bases and acids, and second, those containing the schemes for the analysis of the different unknown solutions. The tables containing the schemes are the ones which the student is likely to use the most; hence they are circumlined with a single heavy-face rule, as shown in section 47. Since the tables of preliminary work for the different groups contain the information that leads up to an intelligent grasp and use of the schemes and are not used as frequently as are the schemes, they are circumlined with a double light-face rule, as shown in section 38. The student will find this little ruling device a time-saver later on in the year.

37. Caution.—The results given in the following table are those obtained when all the conditions of the experiment are favorable. It is well to remember, however, that a slight variation in the conditions, *e.g.* temperature, concentration or dilution of solutions, too little or too much of the reagent, the incidental presence of an acid or an alkali, may affect the experiment to such an extent that the results given in the table may appear only to a slight extent or even not at all. It is of the greatest importance, therefore, that the student should agree with himself to see results *exactly* as they present themselves, and refuse to allow himself to be prejudiced in his observation by what the book says. In this connection reread the fourth requirement for successful work in Qualitative Analysis as given in section 3 and the illustration given in section 4.

38. Table of Preliminary Work for Group II				
Reagent	Barium $\text{BaCl}_2 + \text{Aq}$	Strontium $\text{SrCl}_2 + \text{Aq}$	Calcium $\text{CaCl}_2 + \text{Aq}$	Magnesium $\text{MgSO}_4 + \text{Aq}$
$(\text{NH}_4)_2\text{CO}_3 + \text{Aq.}$	Immed., white ppt., BaCO_3 ; sol. in dil. HCl ; insol. in NH_4Cl .	Immed., white ppt., SrCO_3 ; sol. in dil. HCl ; insol. in NH_4Cl .	Immed., white ppt., CaCO_3 ; sol. in dil. HCl ; insol. in NH_4Cl .	Slow, white ppt., basic Mg carbonate, $\text{MgCO}_3 \cdot \text{MgO}_2\text{H}_2$; sol. in dil. HCl ; sol. in $\text{NH}_4\text{Cl} + \text{Aq.}$
$\text{NH}_4\text{OH.}$	No ppt.	No ppt.	No ppt.	White ppt., MgO_2H_2 ; sol. in $\text{NH}_4\text{Cl} + \text{Aq.}$
H_2SO_4 Dil.	Immed., white ppt., BaSO_4 ; insol. in H_2O and in dil. HCl .	Slow, white ppt., SrSO_4 ; very sl. sol. in H_2O ; insol. in dil. HCl .	Slow, white ppt., CaSO_4 ; somewhat sol. in H_2O ; insol. in dil. HCl .	No ppt.
$(\text{NH}_4)_2\text{SO}_4 + \text{Aq.}$	Immed., white ppt., BaSO_4 .	Immed., white ppt., SrSO_4 .	Slow, white ppt., CaSO_4 .	No ppt.
$\text{K}_2\text{CrO}_4 + \text{Aq.}$	Immed., yellow ppt., BaCrO_4 ; sol. in considerable dil. HCl .	No ppt. in dil. soln.; very slow, yellow ppt., SrCrO_4 , in conc. soln.; sol. in HCl .	No ppt.	No ppt.
$(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{Aq.}$	Immed., white ppt., BaC_2O_4 ; sol. in dil. HCl ; sl. sol. in $\text{HC}_2\text{H}_3\text{O}_2$.	Immed., white ppt., SrC_2O_4 ; sol. in dil. HCl ; sl. sol. in $\text{HC}_2\text{H}_3\text{O}_2$.	Immed., white ppt., CaC_2O_4 ; sol. in considerable HCl ; insol. in $\text{HC}_2\text{H}_3\text{O}_2$.	No ppt. in dil. soln.
$\text{Na}_2\text{HPO}_4 + \text{Aq.}$	Immed., white ppt., BaHPO_4 ; sol. in dil. HCl .	Immed., white ppt., SrHPO_4 ; sol. in dil. HCl .	Immed., white ppt., CaHPO_4 ; sol. in dil. HCl .	Slow, white ppt., MgHPO_4 ; sol. in dil. HCl .
Flame Coloration.	Yellowish green.	Red.	Orange.	—

39. Equations for Group II Preliminary Work. — The following list contains the equations for all the reactions taking place in the preliminary work for Group II indicated in the preceding table.

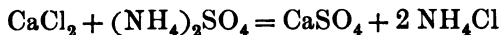
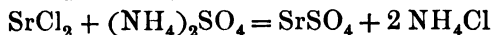
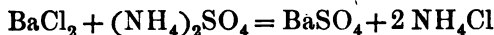
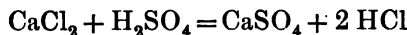
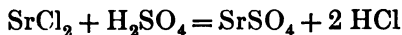
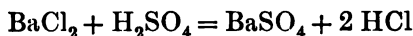
40. Carbonates.



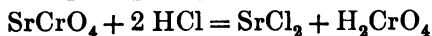
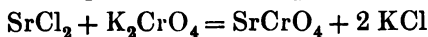
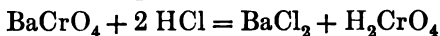
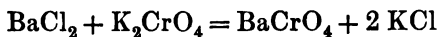
41. Hydrates.

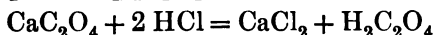
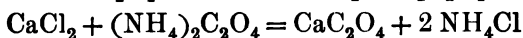
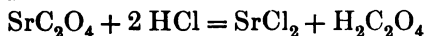
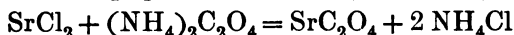
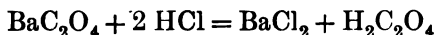
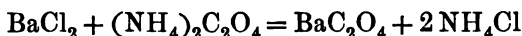
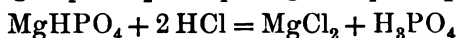
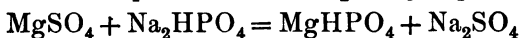
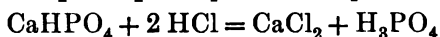
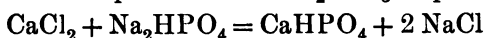
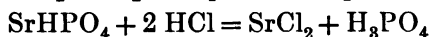
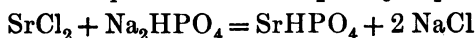
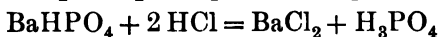
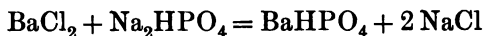


42. Sulphates.



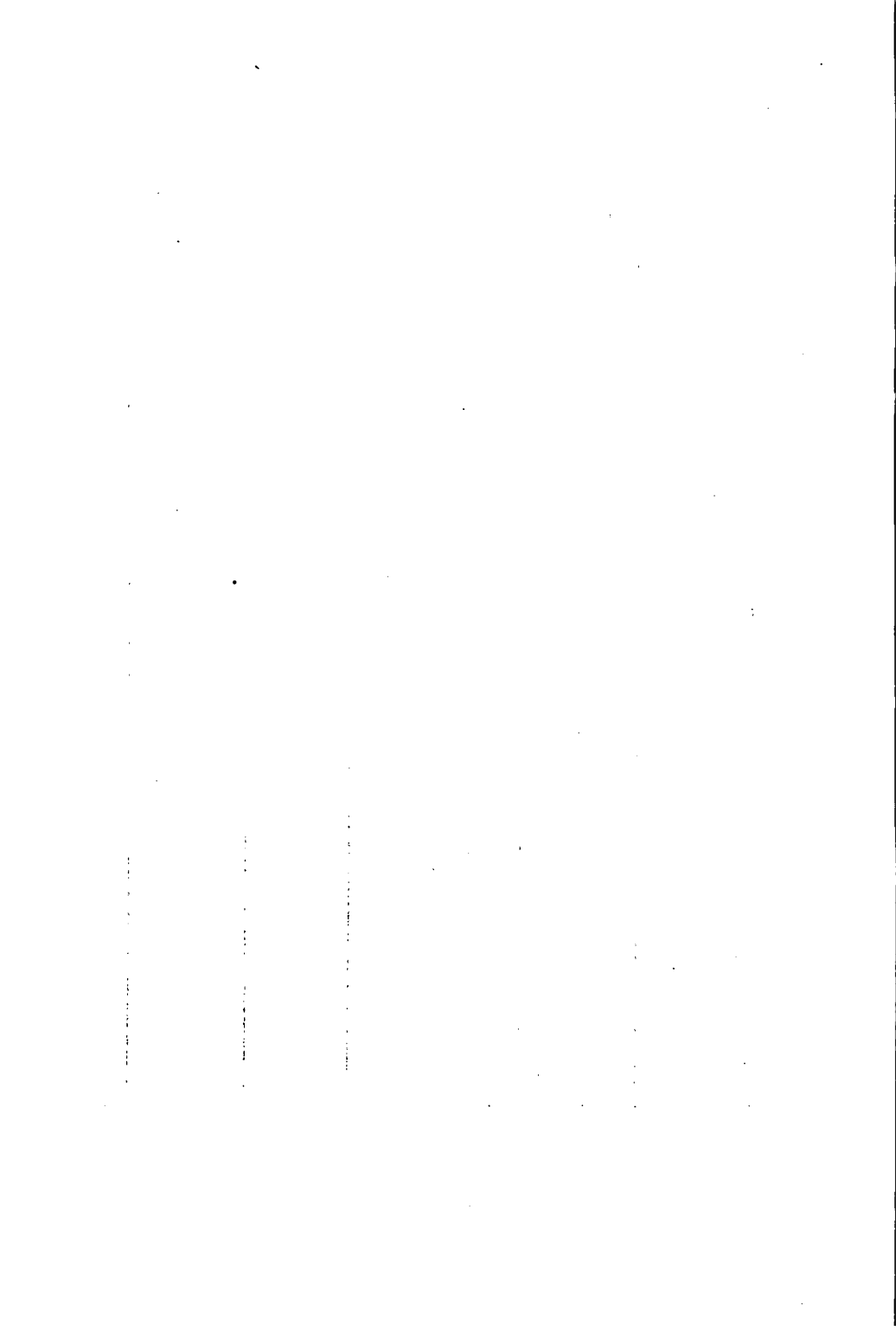
43. Chromates.



44. Oxalates.**45. Phosphates.**

46. The Known Solution on Group II. — A known solution containing Ba, Sr, Ca, and Mg should be analyzed carefully according to the scheme for Group II. All steps should be considered thoughtfully, and under no circumstances should a reagent be added unless the reason for its addition is clearly understood. Questions arising in this work are usually answered in the notes immediately following the scheme. It is well to write up in the laboratory notebook a very full account of the analysis of the known solution recording all the details. This will be found valuable for reference in later work. The ability to go through the known solution according to the scheme and get every result sharply and accurately will facilitate greatly the examination of unknown solutions. After such a careful analysis of the known solution for Group II, the student should be able to analyze the next few solutions with only an occasional reference to the printed scheme, and finally, to get along entirely without the printed scheme.

[illegible]



48. Notes on Scheme for Group II. — The following notes will be found of service in the analysis of a solution for Group II because they give the reasons for the different steps of the procedure, and point out hidden snags that are likely to make the solution “go wrong.”

49. Enough NH_4Cl should be added to prevent the Mg from precipitating with the carbonates. A large excess should be avoided, however, because the carbonates of the alkaline-earth metals are slightly soluble in $\text{NH}_4\text{Cl} + \text{Aq}$, particularly if the mixture is boiled. Some idea of the proper amount can be obtained by adding different amounts of $\text{NH}_4\text{Cl} + \text{Aq}$ to equal portions of a Mg solution, and then adding $(\text{NH}_4)_2\text{CO}_3 + \text{Aq}$ and noting how much NH_4Cl is necessary to just prevent precipitation.

50. NH_4OH is added till the solution is slightly alkaline, because the solution might be acid, and the carbonates are not precipitated from an acid solution. The alkalinity of the solution may be shown by the odor or by testing with turmeric paper, but the solution must be well shaken before testing, to insure complete mixing of the reagent with the solution.

51. The solution should be heated almost to boiling to render the precipitate granular, but it should not be actually boiled on account of the slight solubility of the carbonates in hot NH_4Cl solution.

52. Complete precipitation can readily be recognized by allowing the precipitate to settle, tipping the beaker a little, and letting a few drops of the reagent run down the side of the beaker; if a precipitate forms when the reagent strikes the clear liquid, then enough had not been added originally, and more must be added till a few drops extra cause no further precipitate.

53. Dissolve in HNO_3 on the filter paper by adding a few c.c. of dilute HNO_3 directly to the precipitate on the filter paper. As the filtrate runs through catch it in a test tube, and if the precipitate has not all dissolved, pour the filtrate back upon the filter and let it run through again.

54. A large excess of HNO_3 in dissolving the carbonates should be avoided because the excess must all be expelled by evaporation later.

55. Heat till no more odor of HNO_3 is noticeable, in order to make sure that the nitrates of Ba, Sr, and Ca are perfectly dry. The nitrates of Ba and Sr are easily soluble in water; therefore if they are not completely anhydrous, small quantities will go into solution during treatment with the ether-alcohol mixture and appear in the test for Ca; these two nitrates also absorb moisture from the air; therefore they must be treated immediately with the ether-alcohol mixture. In drying the nitrates, too high a temperature should be avoided, for this decomposes the nitrates to oxides.

56. The ether-alcohol mixture consists of equal portions of ether and of absolute alcohol. Ordinary alcohol is not suitable for this mixture, for it contains enough water to dissolve traces of Ba and Sr nitrates.

57. Dilute with several times its volume of water in order to prevent the precipitation of SrCrO_4 along with BaCrO_4 when K_2CrO_4 is added. Furthermore, the amount of $\text{HC}_2\text{H}_3\text{O}_2$ should be small, and the BaCrO_4 must be precipitated hot, otherwise it is likely to run through the filter.

58. Add K_2CrO_4 to complete precipitation, for if Ba is not completely removed, a little will remain in the solution which is to be tested for Sr, and the subsequent precipitate produced by $(\text{NH}_4)_2\text{CO}_3$ may be mistaken for Sr.

59. To (a) add a little $(\text{NH}_4)_2\text{SO}_4$ in order to precipitate traces of Ba that may have escaped precipitation by $(\text{NH}_4)_2\text{CO}_3$.

60. To (b) add a little $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in order to precipitate traces of Ca that may have escaped precipitation by $(\text{NH}_4)_2\text{CO}_3$.

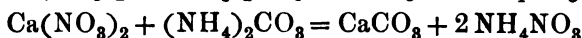
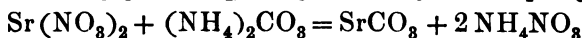
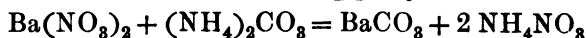
61. Empty (a) into (c); likewise empty (b) into (c); this is to insure complete removal of Ba and Ca before testing the filtrate for Mg.

62. The precipitate of MgNH_4PO_4 is a very delicate test for Mg. The precipitate is slightly soluble in water, but less soluble in NH_4OH ; therefore considerable NH_4OH should be present and the solution should not be too dilute. MgNH_4PO_4 is crystalline and sometimes does not form immediately; therefore it is well to let it stand several hours; rubbing the sides of the test tube with a glass rod helps to start the precipitation. A slight amorphous precipitate produced by Na_2HPO_4 may be a phosphate of Ba, Sr, or Ca, due to traces of these metals escaping precipitation by

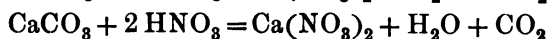
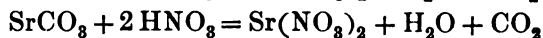
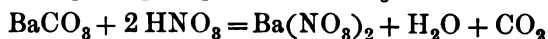
$(\text{NH}_4)_2\text{CO}_3$; in that case make sure that enough $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ were added to remove the traces.

63. Equations for Scheme for Group II.—The following list contains the equations for the reactions taking place in the analysis of a solution containing the four members of Group II.

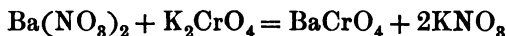
64. Precipitation with $(\text{NH}_4)_2\text{CO}_3$.



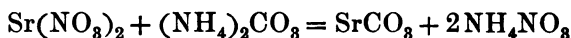
65. Dissolving the precipitate in HNO_3 .



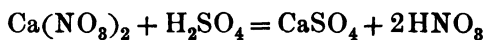
66. Removing Ba.



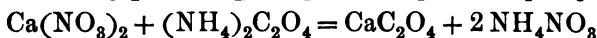
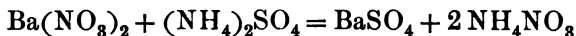
67. Test for Sr.



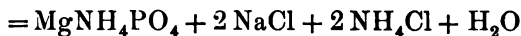
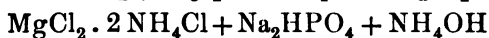
68. Test for Ca.



69. Removal of traces of Ba and Ca.



70. Test for Mg.



71. Laboratory Notes on Unknown Solutions.—In order to save time in writing up the notes on the unknown solutions, it is well to use any condensed form that will show the principal steps in the analysis together with the results which show the

presence or absence of each member. The record should be made at the time the solution is analyzed; if written up later, when the facts have become cold, it is generally incomplete and often unreliable. In fact, it is better to write up the record step by step during the analysis; this tends to make judgment of tests sharp, definite, and prompt; in addition, it lessens the danger of missing indicative reactions or phenomena. It is needless to say that the record should tell what actually happened, and not what you think ought to have taken place. Accurate reports on the unknown solutions should, of course, be the aim in view; yet the fact remains that in Qualitative Analysis, as in other fields, it is difficult for the beginner to be totally correct from the start. It is also well known that we often learn more from our mistakes than from our successes. It follows, therefore, that a record which appears wrong when compared with the book, but which is probably right for the conditions obtaining at the time of the experiment, is much more reliable than a transcript from the book.

72. Sample Page from Laboratory Notebook. — The following sample page from a laboratory notebook is given merely as a

SOLUTION NO. XYZ

+ NH_4Cl , NH_4OH in exc. Heat, + $(\text{NH}_4)_2\text{CO}_3$, White ppt.
 Filter. F. + $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, Na_2HPO_4 , White ppt. **Mg** pres.
 P. + HNO_3 . Evap. Dry. + ether-alcohol, filter.
 F. + H_2SO_4 White ppt. **Ca** pres.
 R. Wash. + $\text{HC}_2\text{H}_3\text{O}_2$, K_2CrO_4 Yellow ppt. **Ba** pres.
 Filter. F. + NH_4OH , $(\text{NH}_4)_2\text{CO}_3$ White ppt. **Sr** pres.
 ∴ **Ba**, **Sr**, **Ca**, **Mg** present.

suggestion, and need not be followed exactly, if the student prefers some other form which is as clear. Solution XYZ was an unknown solution that was found to contain all four members of the group. The main advantage in the sample page is

that all addition of reagents and similar steps are on one side of the page, while all results that prove a substance present or absent are on the other side.

GROUPS I AND II TOGETHER

73. A solution containing Groups I and II together is analyzed in much the same way that solutions of the groups separately were analyzed. It is treated with NH_4Cl , NH_4OH , and $(\text{NH}_4)_2\text{CO}_3$, as usual, but the filtrate from the precipitated carbonates contains Group I as well as Mg, and from this filtrate the Mg must be separated before the regular tests for Group I can be applied.

74.

Scheme for Groups I and II

To 10 c.c. of the solution containing Groups I and II add NH_4Cl and NH_4OH ; heat and add $(\text{NH}_4)_2\text{CO}_3$. Filter, and save both precipitate and filtrate.

P. White precipitate,

BaCO_3 ,

SrCO_3 ,

CaCO_3 .

Proceed as with the corresponding precipitate in **Scheme for Group II**. See section **47**.

F. Contains Mg and Group I.^o Divide into two parts, — (a) the smaller and (b) the larger.

To (a) add

Na_2HPO_4 .^o

White precipitate,

MgNH_4PO_4 .

∴ **Mg pres.**

To remove Mg^{2+} before testing for Group I, evaporate (b) to dryness and expel the NH_4 salts^o by heating till white fumes of NH_4 salts are all gone. Dissolve in a little water and add $\text{BaO}_2\text{H}_2 + \text{Aq}$ in slight excess.

P. White precipitate, MgO_2H_2 . Reject.

F. Contains BaCl_2 and Group I. Remove Ba by adding NH_4OH , heating, and adding $(\text{NH}_4)_2\text{CO}_3$. Filter.

P. White precipitate, BaCO_3 . Reject.

F. Contains Group I. Evaporate to dryness and try flame test for Na, K, and Li.

Test in the original solution with CaO_2H_2 for NH_4 .

75. Notes on Scheme for Groups I and II Together.—The following notes will be found of service in the analysis of a solution for Groups I and II; they refer mainly to the separation of the two groups from each other. The notes given under Group I and under Group II all hold here and should be consulted in case of trouble.

76. The solution containing Mg and Group I may to advantage be tested with the platinum wire from time to time during the evaporation to dryness. When the Mg is in solution, it does not interfere so much with the flame test for Group I as when dry, but small quantities of the latter may not show up till the solution becomes concentrated.

77. Add Na_2HPO_4 .—Consult note on test for Mg under Scheme for Group II; this note is in section 62.

78. The removal of Mg before testing for Group I is advisable because dry Mg salts impart a slight yellow color to the flame that resembles the Na flame; hence much Mg in the dry residue is likely to interfere with the flame test for the alkali metals, or obscure them entirely if the latter are present in small quantity only.

79. Expel the NH_4 salts because Mg will not be precipitated by BaO_2H_2 in the presence of NH_4 salts.

GROUPS III AND IV. Al, Cr, Fe, Co, Ni, Mn, Zn

80. List of Members.—The members of Group III are :

Al	Aluminium.
Cr	Chromium.

and those of Group IV are :

Fe	Iron.
Co	Cobalt.
Ni	Nickel.
Mn	Manganese.
Zn	Zinc.

These two groups will be considered together because there is no reagent which will separate the two groups from each other conveniently and satisfactorily.

81. Preliminary Work.—Take in separate test tubes about 10 c.c. each of solutions of $\text{Al}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3$, FeSO_4 (ferrous sulphate), $\text{Fe}(\text{NO}_3)_3$ (ferric nitrate), $\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$, and $\text{Zn}(\text{NO}_3)_2$. These solutions should all be of a strength 1:40 except $\text{Ni}(\text{NO}_3)_2$ which should have a strength of 1:10. To each solution add a little $\text{NaOH} + \text{Aq}$, drop by drop, being careful that the NaOH is not in excess. Note the precipitate formed in each case, particularly its color and its form. It is well to shake each test tube to aid the precipitation. Then add a considerable excess of NaOH to each test tube and note whether the precipitate dissolves. Repeat this work, using NH_4OH , $(\text{NH}_4)_2\text{S}$, and BaCO_3 as reagents, and verify all the results in the following table. The BaCO_3 emulsion should be shaken before it is added, and there should be a distinct line of separation between the excess of BaCO_3 powder and the hydrate formed. In dissolving the sulphides in HCl any faint grayish precipitate that may be left is probably precipitated sulphur and may be discarded. Before doing this preliminary work the student should again give heed to the caution given in connection with the preliminary work for Group II. This caution, on account of its importance, is here reprinted in full. **Caution:** The results given in the following table are those obtained when all the conditions of the experiment are favorable. It is well to remember, however, that a slight variation in the conditions, *e.g.* temperature, concentration or dilution of solutions, too little or too much of the reagent, the incidental presence of an acid or an alkali, may affect the experiment to such an extent that the results given in the table may appear only to a slight extent or even not at all. It is of the greatest importance, therefore, that the student should agree with himself to see results *exactly* as they present themselves, and refuse to allow himself to be prejudiced in his observation by what the book says. In this connection re-read the fourth requirement for successful work in Qualitative Analysis as given in section 3 and the illustration given in section 4.

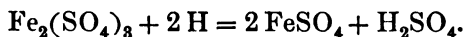
82.		Table of Preliminary Work		
Reagent	Aluminium $\text{Al}(\text{NO}_3)_3 + \text{Aq}$	Chromium $\text{Cr}(\text{NO}_3)_3 + \text{Aq}$	Ferrous Iron $\text{FeSO}_4 + \text{Aq}$	Ferric Iron $\text{Fe}(\text{NO}_3)_3 + \text{Aq}$
NaOH + Aq not in excess.	White, gelatinous ppt., AlO_2H_3 ; sol. in excess to AlO_2Na_3 .	Green or grayish blue, gelatinous ppt., CrO_2H_3 ; sol. in excess to green solution; repptd. by boiling.	Gelatinous ppt., FeO_2H_2 ; white or light green at first; turns dark green, then red-brown; insol. in excess.	Red-brown, gelatinous ppt., FeO_2H_3 ; insol. in excess.
NH_4OH + Aq not in excess.	White, gelatinous ppt., AlO_2H_3 ; sl. sol. in excess; sol. in dil. HCl .	Green or grayish blue, gelatinous ppt., CrO_2H_3 ; sl. sol. in excess to a red solution; sol. in dil. HCl .	Gelatinous ppt., FeO_2H_2 ; white or light green at first; turns dark green, then red-brown; insol. in excess; sol. in dil. HCl .	Red-brown, gelatinous ppt., FeO_2H_3 ; insol. in excess; sol. in dil. HCl .
NH_4Cl and NH_4OH .	White, gelatinous ppt., AlO_2H_3 .	Green or grayish blue, gelatinous ppt., CrO_2H_3 .	Light green, gelatinous ppt., FeO_2H_2 .	Red-brown, gelatinous ppt., FeO_2H_3 .
$(\text{NH}_4)_2\text{S}$ + Aq not in excess.	White, gelatinous ppt., AlO_2H_3 ; sol. in dil. HCl .	Green or grayish blue, gelatinous ppt., CrO_2H_3 ; sol. in dil. HCl .	Black ppt., FeS ; sol. in dil. HCl .	Black ppt., $\text{FeS} (+\text{S})$; sol. in dil. HCl .
H_2S .	No ppt.	No ppt.	No ppt. in acid solution.	Reduced to a ferrous salt with separation of S .
BaCO_3 + Aq .	White, gelatinous ppt., AlO_2H_3 .	Green or grayish blue, gelatinous ppt., CrO_2H_3 .	White ppt., BaSO_4 .	Red-brown ppt., FeO_2H_3 .

for Groups III and IV

Cobalt $\text{Co}(\text{NO}_3)_2 + \text{Aq}$	Nickel $\text{Ni}(\text{NO}_3)_2 + \text{Aq}$	Manganese $\text{Mn}(\text{NO}_3)_2 + \text{Aq}$	Zinc $\text{Zn}(\text{NO}_3)_2 + \text{Aq}$
Blue, gelatinous basic ppt.; turns grayish pink, CoO_2H_2 when heated; insol. in excess.	Light green, gelatinous ppt., NiO_2H_2 ; insol. in excess.	Light brown, gelatinous ppt., MnO_2H_2 ; insol. in excess.	White, gelatinous ppt., ZnO_2H_2 ; sol. in excess to ZnO_2Na_2 .
Blue, gelatinous basic ppt.; sol. in excess to a red solution; sol. in dil. HCl.	Light green gelatinous ppt., NiO_2H_2 ; sol. in excess to a blue solution; sol. in dil. HCl.	Light brown, gelatinous ppt., MnO_2H_2 ; turns dark brown; insol. in excess; sol. in dil. HCl.	White, gelatinous ppt., ZnO_2H_2 ; sol. in excess; sol. in dil. HCl.
No ppt.	No ppt.	No ppt.	No ppt.
Black ppt., CoS ; insol. in dil. HCl; sol. in hot, conc. HCl or aqua regia.	Black ppt., NiS ; sl. sol. in excess to a brown solution; insol. in dil. HCl; sol. in hot, conc. HCl or aqua regia.	Flesh-colored ppt., MnS ; sol. in dil. HCl.	White ppt., ZnS ; sol. in dil. HCl.
No ppt. in acid solution; black CoS in neutral or alkaline solution.	No ppt. in acid solution; black NiS in neutral or alkaline solution.	No ppt. in acid solution; flesh-colored MnS in neutral or alkaline solution.	No ppt. in mineral acid solution; white ZnS in neutral, alkaline, or acetic acid solution.
No ppt.	No ppt.	No ppt.	No ppt.

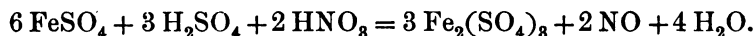
83. "Ferrous" and "Ferric" Iron. — Iron exists in two states, — the ferrous or slightly oxidized state, and the ferric or highly oxidized state. FeCl_2 , $\text{Fe}(\text{NO}_3)_2$, and FeSO_4 are ferrous chloride, ferrous nitrate, and ferrous sulphate respectively, while the corresponding ferric salts are FeCl_3 , $\text{Fe}(\text{NO}_3)_3$, and $\text{Fe}_2(\text{SO}_4)_3$. The most convenient ferrous salt to use is FeSO_4 , and $\text{Fe}(\text{NO}_3)_3$ is a convenient ferric salt. Ferrous salts usually have a tendency to oxidize to the corresponding ferric salts on being exposed to the air, and the ferric salts may be reduced to ferrous salts by proper reducing agents. The reduction of ferric sulphate to ferrous sulphate and the oxidation of ferrous sulphate to ferric sulphate are considered in the following paragraphs.

84. Reduction of an Iron Solution from Ferric to Ferrous State. — Select good clear crystals of ferrous sulphate, FeSO_4 . Wash off with a little water as much as possible of the coating of ferric sulphate that always forms when FeSO_4 stands for any length of time. Then dissolve the crystals in distilled water, heating a little if necessary. If the solution is clear and has a green color, only ferrous sulphate is present. More likely the solution will be somewhat cloudy, due to the presence of some ferric sulphate, which does not dissolve as readily as the ferrous sulphate. Boiling the solution generally changes the ferrous salt to the ferric salt, the solution becoming brownish and cloudy. If the solution is cloudy, add a little dilute H_2SO_4 and heat gently till the solution becomes clear and green. If the solution does not clear up readily, add a few clean iron filings; the nascent hydrogen evolved reduces the ferric sulphate to ferrous sulphate.



85. Oxidation of an Iron Solution from Ferrous to Ferric State. — To a little of the freshly reduced ferrous sulphate solution made in section 84 add a few drops of concentrated nitric acid and heat a little. Under these conditions the nitric acid is reduced to NO and H_2O , liberating some free oxygen which oxidizes the iron from the ferrous to the ferric state; nitric acid is therefore

considered a good oxidizing agent. If the ferrous solution was concentrated, the resulting ferric sulphate solution may be dark red. In that case dilute with a little water and compare the color with that of the ferrous sulphate solution started with.



86. Tests for Iron. — To equal portions of freshly reduced FeSO_4 and of $\text{Fe}(\text{NO}_3)_3$ add small portions of $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{K}_6\text{Fe}_2(\text{CN})_{12}$, and KSCN , and verify the results in the following table. From these results pick out those tests that show conclusively which state of iron is present in an unknown solution.

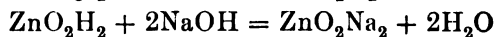
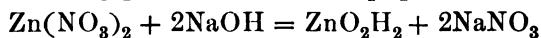
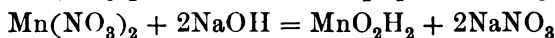
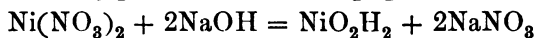
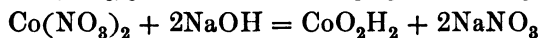
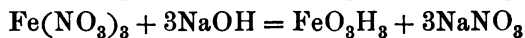
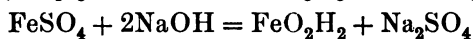
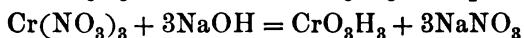
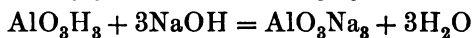
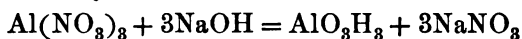
87. Ferrous and Ferric Iron		
Reagents	Ferrous iron $\text{FeSO}_4 + \text{Aq}$	Ferric iron $\text{Fe}(\text{NO}_3)_3 + \text{Aq}$
$\text{K}_4\text{Fe}(\text{CN})_6$, Potassium ferrocyanide.	Light blue precipitate of varying composition.	Dark blue precipitate, fer- ric ferrocyanide, "Prussian Blue," $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$; insol. in HCl ; decomp. by NaOH .
$\text{K}_6\text{Fe}_2(\text{CN})_{12}$, Potassium ferricyanide.	Dark blue precipitate, fer- rous ferricyanide, "Turn- bull's Blue," $\text{Fe}_3\text{Fe}_2(\text{CN})_{12}$; insol. in HCl ; decomp. by NaOH .	No precipitate forms, but the solution is often col- ored brown.
KSCN , Potassium sulphocyanide.	No precipitate and no coloration. A red-brown solution is often obtained because a trace of ferric iron has been left in solution.	Blood-red coloration caused by the formation of $\text{Fe}(\text{SCN})_3$. An excellent test for small quantities of ferric iron.

88. With a ferrous solution potassium ferricyanide gives a dark blue precipitate. With a ferric solution potassium ferrocyanide gives a dark blue precipitate. Note that in the preceding lines the heavy-faced letters give a key to what are considered the best reagents to add to show which state of iron is present in an unknown solution.

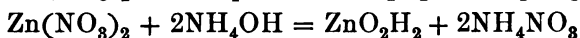
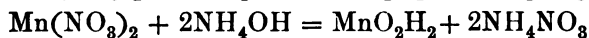
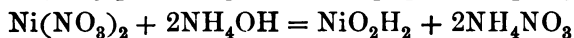
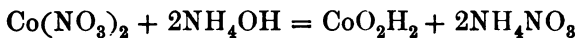
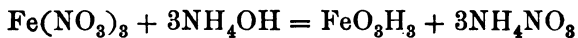
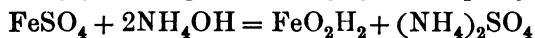
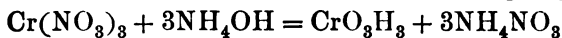
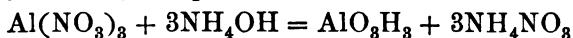
89. Try the proper tests for ferrous and ferric iron in the solution obtained in section **84** and see if the reduction was complete ; also try the proper tests for ferrous and ferric iron in the solution obtained in section **85** and see if the oxidation was complete.

90. Equations for Preliminary Work for Groups III and IV.
— The following list contains the equations for all the reactions taking place in the preliminary work for Groups III and IV indicated in the preceding table.

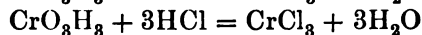
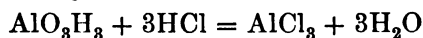
91. Hydrates by NaOH.

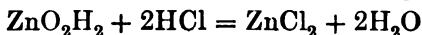
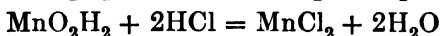
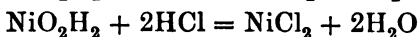
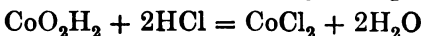
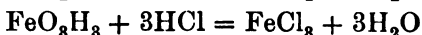
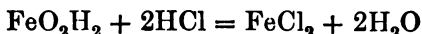


92. Hydrates by NH_4OH .

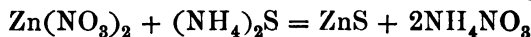
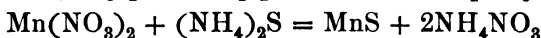
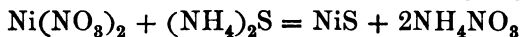
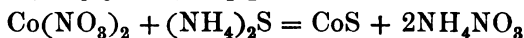
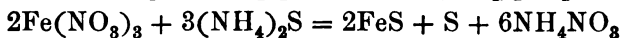
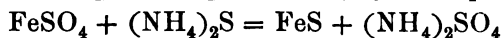
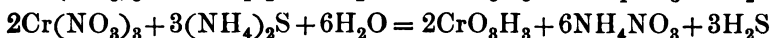
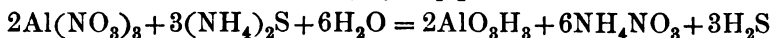


93. Solution of hydrates in HCl.

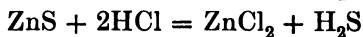
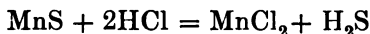
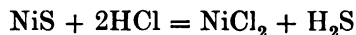
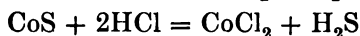
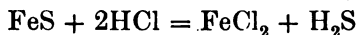
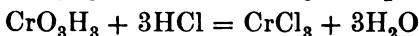
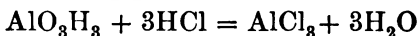




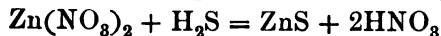
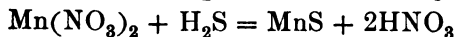
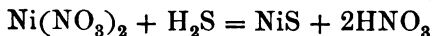
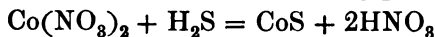
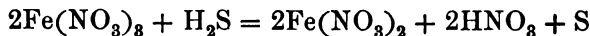
94. Precipitates caused by $(\text{NH}_4)_2\text{S}$.



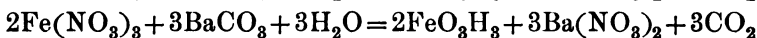
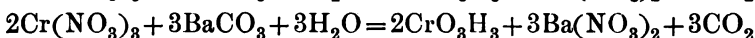
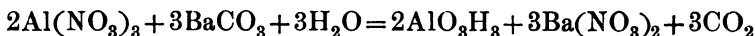
95. Dissolving $(\text{NH}_4)_2\text{S}$ precipitates in HCl .



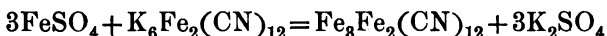
96. Precipitates caused by H_2S .



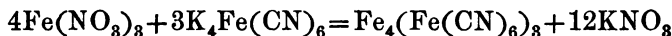
97. Precipitates caused by $\text{BaCO}_3 + \text{Aq.}$



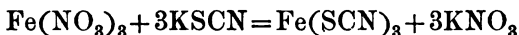
98. Test for *ous* Fe.



Test for *ic* Fe.



Test for trace of Fe.



99. The Known Solution on Groups III and IV. — Two known solutions should be analyzed for Groups III and IV, the first one containing Al, Fe, Co, Ni, Mn, and Zn, and the second containing all these with the addition of Cr. That part of the scheme in section **100** should be used for both solutions ; for the rest of the first solution use **A** of the scheme (section **101**) and for the rest of the second solution use **B** of the scheme (section **102**). The complete analysis of a solution for Groups III and IV is included in sections **100** and **102** ; if Cr is absent, the work may be greatly simplified and part **A** may be substituted for part **B**. All steps should be considered thoughtfully, and under no circumstances should a reagent be added unless the reason for its addition is clearly understood. Questions arising in this work are usually answered in the notes immediately following the scheme. It is well to write up in the laboratory notebook a very full account of the analysis of the known solutions, recording all the details. The ability to go through the known solutions and get every result sharply and accurately will facilitate greatly the examination of unknown solutions. It is well to read the scheme through occasionally without referring to the notes at all ; this will help fix in mind the general method of procedure and will offset any tendency to follow the scheme mechanically.

100.

Scheme for Groups III and IV

Put in a 250 c.c. flask 10 c.c. of the solution containing Al, Cr, Fe, Co, Ni, Mn, and Zn. Add about 20 c.c. $\text{NH}_4\text{Cl}^\circ$ and then enough NH_4OH to make it slightly alkaline^o or to cause a slight precipitate;^o the color of the precipitate often throws considerable light upon the presence or absence of certain members of the group. Then add $(\text{NH}_4)_2\text{S}^\circ$ to complete precipitation.^o Heat to boiling and shake occasionally for 10 or 15 minutes or till precipitate is granular. Filter through a plaited filter^c as rapidly as possible,^o and wash with hot water^c containing a few drops of $(\text{NH}_4)_2\text{S}$.

P. Contains^o AlO_3H_3 , CrO_3H_3 , FeS , CoS , NiS , MnS , and ZnS . Pour cold dilute HCl° on the precipitate in the filter paper, break the paper at the point, and wash the mixture down into a beaker with as little water as possible. Let stand for a few minutes; then filter.

Residue^o is CoS and NiS (with traces of FeS and S).

F. May contain FeCl_2 , MnCl_2 , ZnCl_2 , AlCl_3 , and CrCl_3 .

Test a little of the residue with borax bead^o.

Outer flame, blue bead; inner flame, blue bead.

\therefore **Co pres.** Ni may be.

Outer flame, red-brown bead; inner flame, gray bead.^o

\therefore **Co abs.** Ni pres.

Outer flame, colorless bead; inner flame, colorless bead.

\therefore **Co and Ni abs.** and the residue was FeS .

If Co is present, dissolve the rest of the residue in a little hot aqua regia^o on the filter paper. Dilute with a little water and add NH_4OH in excess to get rid of Fe. Filter.

P. Red-brown, FeO_3H_3 ; reject.

F. Contains CoCl_2 , NiCl_2 , and NH_4 salts. Evaporate to dryness and expel NH_4 salts.^o Dissolve the residue in a very little aqua regia. Evaporate to a few drops. Add 50 c.c. KNO_3 solution; then add $\text{HC}_2\text{H}_3\text{O}_2$ till strongly acid. Let stand some hours. Filter.

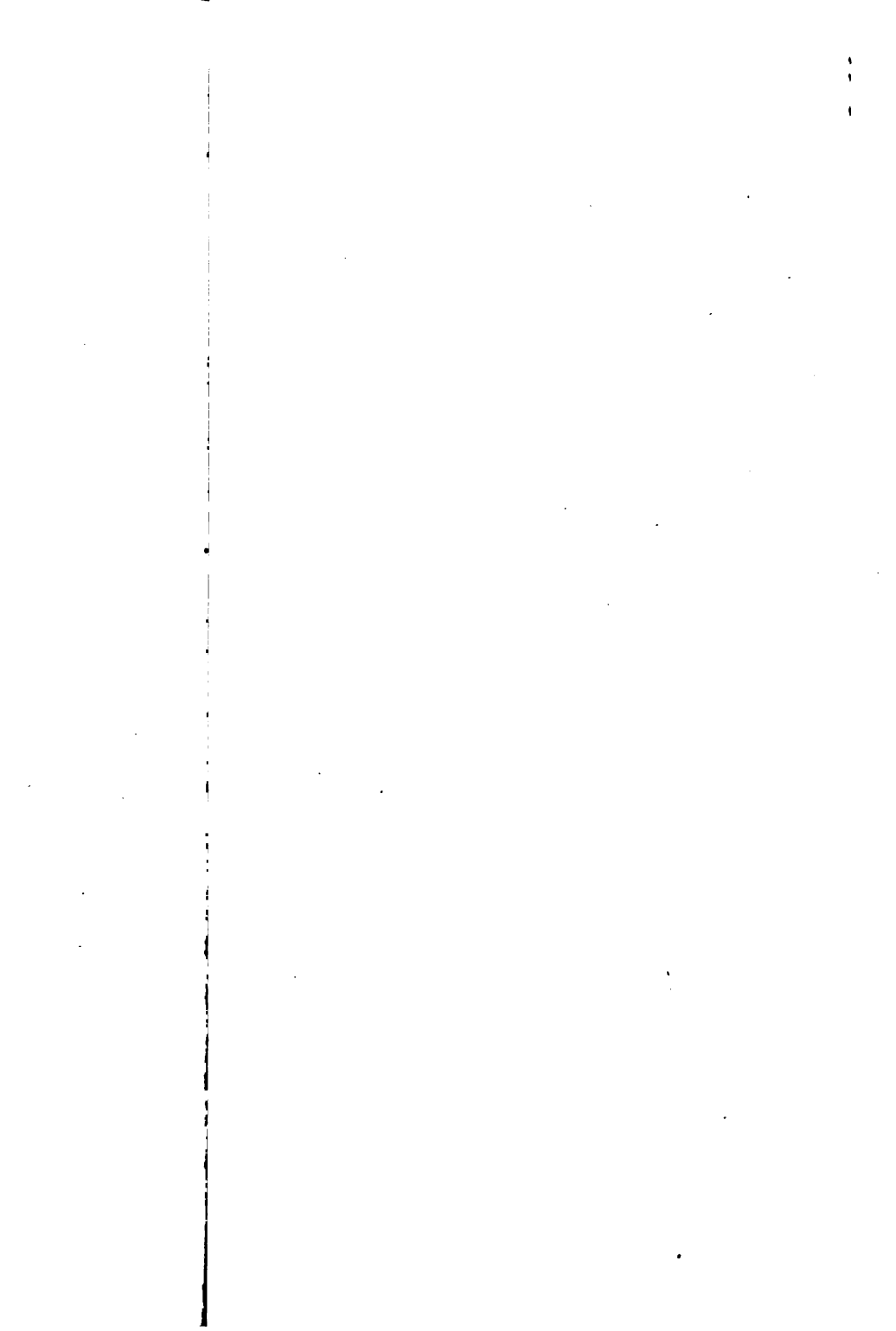
P. Yellow-brown, $\text{Co}(\text{NO}_2)_3 \cdot 3\text{KNO}_2$.^o
 \therefore **Co pres.**

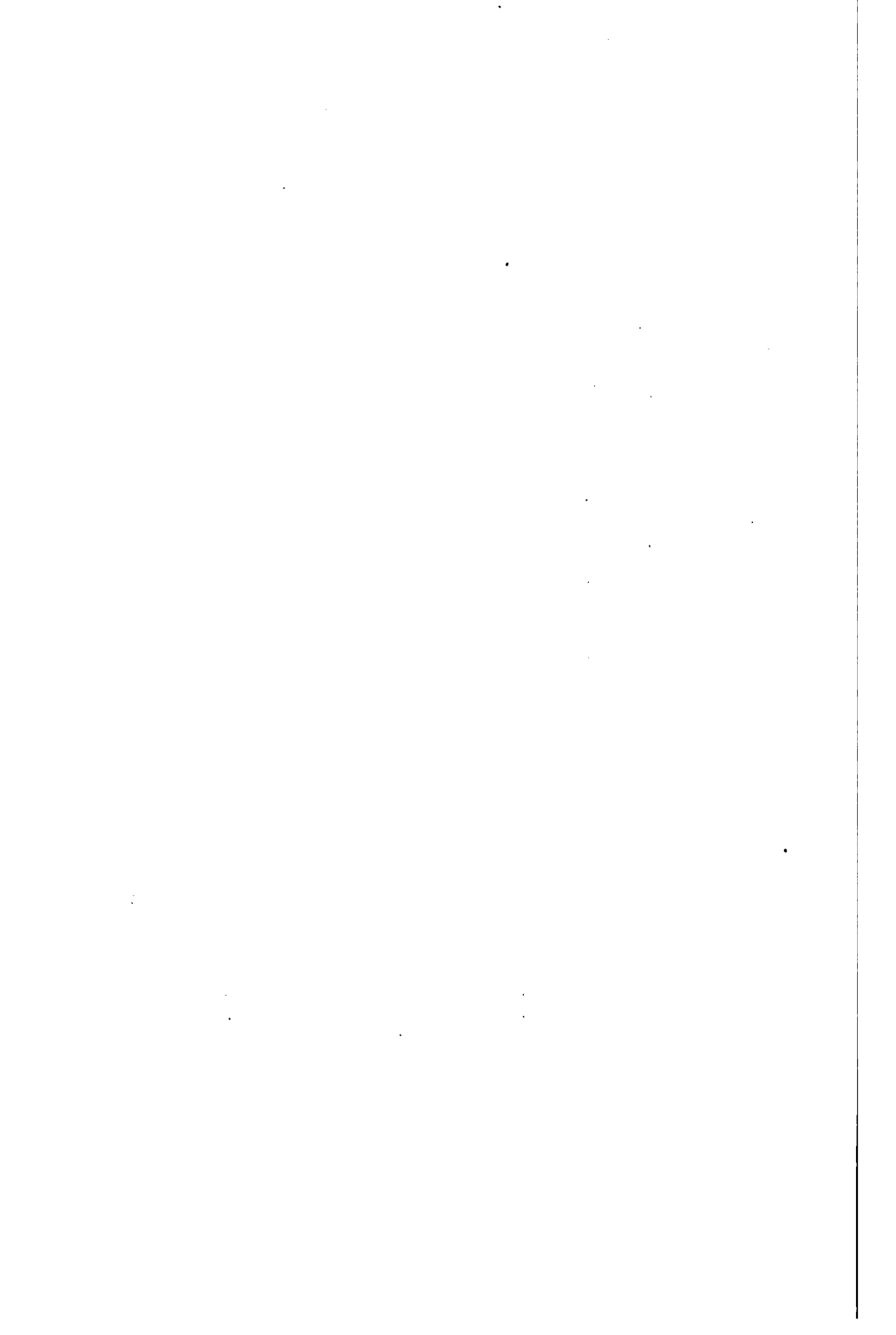
F. Contains NiCl_2 . Add NaOH till alkaline. Light green precipitate, NiO_2H_2 . Test in borax bead. Outer flame, red-brown bead; inner flame, gray bead.
 \therefore **Ni pres.**

If the solution is colorless, Cr is absent. Proceed as in **A**.^o

If the solution is green or purple, Cr is present. Proceed as in **B**.

101. A of Scheme for Groups III and IV			
<p>Solution contains FeCl_2, MnCl_2, ZnCl_2, and AlCl_3. Boil till H_2S is all expelled.° Add a little HNO_3, and boil to convert ferrous Fe to ferric.° Evaporate nearly to dryness to get rid of free acid;° dilute with a little water; add NaOH° till alkaline to test paper, and then add about 10 c.c. more of NaOH.° Filter.</p>			
P. FeO_3H_3 and MnO_2H_2 .°		F. Contains Na_2ZnO_2 and Na_3AlO_3 . Halve the solution into (a) and (b).	
<p>Dissolve a little of the mixed hydrates in dilute HCl. Dilute with water° and add a few drops $\text{K}_4\text{Fe}(\text{CN})_6$. Precipitate is dark blue,° $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. \therefore Fe pres. If Fe is present, test small portions of the original solution with $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}_2(\text{CN})_{12}$ to find out which kind of Fe is present.</p>	<p>Mix the rest of the precipitate with six times as much dry Na_2CO_3 and fuse° on the platinum foil to a thin liquid. Let it cool. Mass is green from the Na_2MnO_4 formed. \therefore Mn pres.</p>	<p>Into (a) pass a little H_2S.° White precipitate, ZnS.° \therefore Zn pres.</p>	<p>Make (b) acid with HCl. Add NH_4OH till alkaline.° Heat a little, and if no precipitate appears, let it stand for half an hour. Precipitate is white and flocculent.° Collects slowly. AlO_3H_3. \therefore Al° pres.</p>





103. Notes on Scheme for Groups III and IV.—The following notes will be found of service in the analysis of a solution for Groups III and IV because they give the reasons for the different steps of the procedure, point out hidden snags, and explain in detail such mechanical processes as have not already been employed.

104. Add NH_4Cl to prevent the precipitation of the hydrates of Co, Ni, Mn, and Zn by NH_4OH , and to insure complete precipitation of AlO_3H_3 , which is slightly soluble in NH_4OH , but insoluble in NH_4Cl . When the solution started with has a strength of 1 : 10, about twice its volume of NH_4Cl + Aq will prevent the precipitation of the hydrates of Co, Ni, Mn, and Zn.

105. Add NH_4OH till slightly alkaline in order to neutralize any free acid that may be present; the preliminary work showed that the hydrates and sulphides of Groups III and IV are soluble in acids and therefore cannot be precipitated from an acid solution.

106. NH_4OH precipitates AlO_3H_3 , CrO_3H_3 and FeO_3H_3 . The color shows which is present, — Al white, Cr green, and Fe green or red-brown, — but this test is reliable only when Fe is absent or present in small quantity only, as the FeO_3H_3 covers up the Al and Cr hydrates. If NH_4OH gives no precipitate, then Fe, Al, and Cr are absent and subsequent search for them may be omitted. In this case only enough NH_4OH should be added to render the solution alkaline.

107. The $(\text{NH}_4)_2\text{S}$ used should be colorless or nearly so, for if yellow $(\text{NH}_4)_2\text{S}_2$ is used, it is likely to cause considerable troublesome precipitated sulphur later. For the same reason care should be taken to avoid using an excess of $(\text{NH}_4)_2\text{S}$.

108. Complete precipitation with $(\text{NH}_4)_2\text{S}$ cannot always be tested as easily as complete precipitation of Ba, Sr, and Ca with $(\text{NH}_4)_2\text{CO}_3$ because the precipitated sulphides do not settle as well. Pour a little of the mixture in the flask on a small filter and to the clear filtrate add a few drops of $(\text{NH}_4)_2\text{S}$.

109. A plaited filter is used in filtering off the precipitates caused by $(\text{NH}_4)_2\text{S}$ because the precipitate is usually gelatinous and filters slowly. A plaited filter is made as follows: Fold a circular filter along the diameter AB in Fig. I, and get the doubled paper shown

in Fig. II. Fold the doubled paper along the line CD of Fig. III and get the form shown in Fig. IV. Open once and get Fig. III

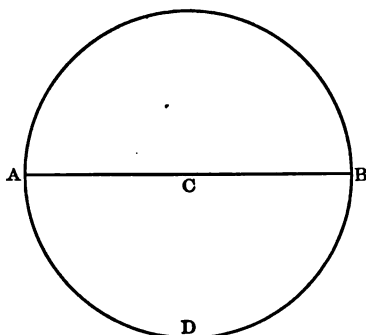


FIG. I

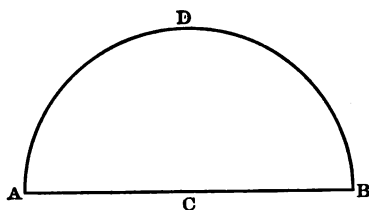


FIG. II

again. Fold along the lines CE and CF of Fig. V so that the edges CA and CB meet each other above CD as in Fig. VI. Open

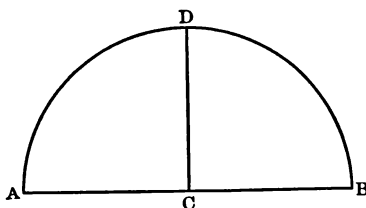


FIG. III

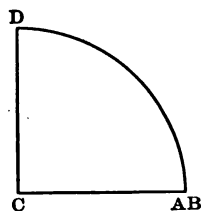


FIG. IV

out once and get Fig. V again. Fold along the lines CG and CH in Fig. VII so that CA shall lie on CE and CB shall lie on CF . Unfold once and get Fig. VII again. Fold along the line CI in

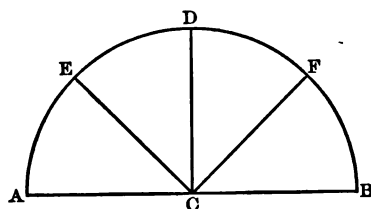


FIG. V

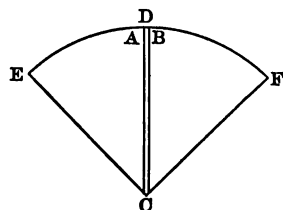


FIG. VI

Fig. VIII so that CE shall lie on CD . Unfold and get Fig. VIII again. Fold along the line CJ in Fig. IX so that CF shall lie on

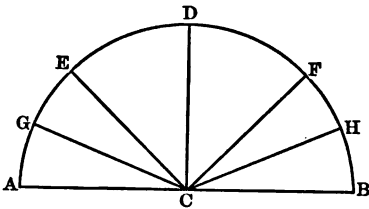


FIG. VII

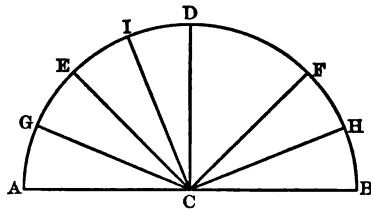


FIG. VIII

CD . Unfold and get Fig. IX again. All the folds made upon the doubled paper now turn to one side so that the paper when

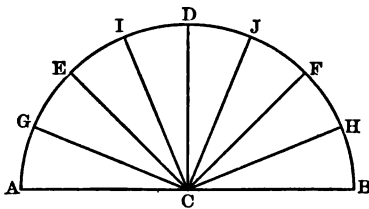


FIG. IX

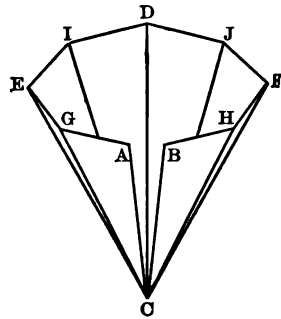


FIG. X

left to itself takes on roughly a conical or funnel shape as in Fig. X. Now turn the paper over and get Fig. XI. Then fold each

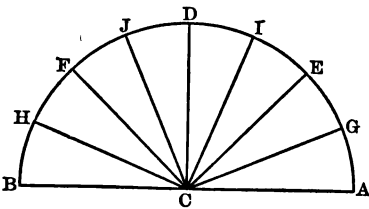


FIG. XI

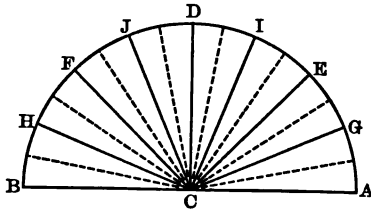


FIG. XII

sector along its middle as indicated by the dotted lines in Fig. XII so that CA shall lie on CG , CG on CE , CE on CI , CI on CD , CD

on CJ , CJ on CF , CF on CH , and CH on CB . The folded paper now roughly resembles a closed fan as in Fig. XIII. Open it out and set it loosely in a funnel, when it should look something like Fig. XIV. Care should be taken when making the folds not to

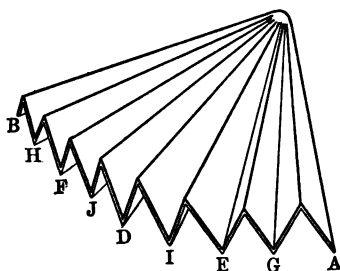


Fig. XIII

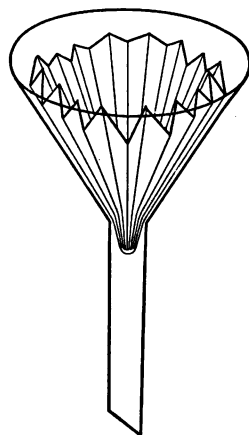


Fig. XIV

crease the folds too sharply at the point C for this is likely to weaken the paper and allow the liquid to break it at the point during filtration. When pouring a hot liquid on a plaited filter, decant it down a rod upon the side of the paper to prevent the hot liquid from bursting the paper.

110. Filter as rapidly as possible because the precipitated sulphides oxidize into sulphates readily on exposure to air. Therefore the heating is done in a flask and the filtering is done rapidly. A small filter paper laid loosely upon the top of the funnel containing the plaited filter will prevent oxidation to some extent. The presence of $(\text{NH}_4)_2\text{S}$ in the wash-water also prevents oxidation.

111. Wash the $(\text{NH}_4)_2\text{S}$ precipitate with hot water to wash out any other salts that might have been in the solution and were not precipitated by $(\text{NH}_4)_2\text{S}$. Before any wash-water is added the precipitate should be allowed to drain entirely free from the solution. Then, using the wash bottle, wash the precipitate down from the sides of the paper into the apex of the filter and stir up the whole with the stream of water. Add a very few drops of

$(\text{NH}_4)_2\text{S}$ to the contents of the filter and allow all liquid to run through.

112. The $(\text{NH}_4)_2\text{S}$ precipitate contains all the members of Groups III and IV, — the former as hydrates, the latter as sulphides. If the precipitate is black, Co, Ni, and Fe are present; if white, Al or Zn, or both; if green, Cr is present probably alone; if flesh-colored, Mn is present probably alone; MnS , however, often turns brown on standing. In all cases confirmatory tests are necessary. If the precipitate is white, of course Fe, Co, and Ni need not be tested for. The AlO_3H_3 and CrO_3H_3 thrown down by NH_4OH are unchanged by $(\text{NH}_4)_2\text{S}$; the FeO_3H_3 is changed to FeS .

113. Cold dilute HCl is used in dissolving the precipitate; otherwise small amounts of CoS and NiS might go into solution and cause trouble in subsequent tests on the filtrate.

114. The black residue from HCl is generally CoS or NiS , or both, and must be tested by the borax bead, because a black residue may be merely a little black FeS inclosed in precipitated S which clots during the previous heating. If the residue imparts no color to the bead, Co and Ni are absent.

115. The borax bead test for Co and Ni is best made this way: Form a loop of one turn at the end of the Pt test wire and heat; dip the hot wire into borax and pick up an amount of borax which will upon fusing fill the loop with a colorless bead. With this bead pick up some of the black precipitate supposed to contain Co or Ni and heat it in the outer or oxidizing flame until the precipitate is seen to float around in the melted bead and to merge finally into the fused mass. Cool and examine the color of the bead. Then heat in the inner or reducing flame; cool and examine the color of the bead again. If the Bunsen burner does not work well, try the blast lamp. The gas flame will probably be colored yellow by the borax; this should not be confounded with the color of the bead.

116. The gray borax bead test for Ni is conclusive only when Co is absent. In such a case no further test is necessary. If the bead is blue, Ni if present is obscured by the Co, and the latter must be removed before testing for Ni. The bead test is very delicate, especially for Co.

117. Aqua regia is made by mixing concentrated HNO_3 and HCl , one part of the former to three parts of the latter. Among other

things formed nascent chlorine is set free and the reaction taking place is said to be: $3 \text{HCl} + \text{HNO}_3 = 2 \text{Cl} + \text{NOCl} + 2 \text{H}_2\text{O}$. When a precipitate is present, however, for the aqua regia to act on, all the Cl is used up in converting the metal into the chloride. Heating aids the reaction. $3 \text{CoS} + 6 \text{HCl} + 2 \text{HNO}_3 = 3 \text{CoCl}_2 + 2 \text{NO} + 4 \text{H}_2\text{O} + 3 \text{S}$. Only the smallest possible quantity of aqua regia should be used, as the excess must usually be evaporated or neutralized later. If the precipitate to be dissolved is on a filter paper, heat a little aqua regia in a test tube and pour it on the filter paper in the funnel. If it does not dissolve all the precipitate as it runs through, heat the filtrate in a test tube and pour it again on the same filter.

118. Expel NH_4 salts before testing for Co and Ni, because Ni is not precipitated completely by NaOH in the presence of NH_4 salts.

119. $\text{Co}(\text{NO}_2)_3 \cdot 3 \text{KNO}_2$, cobaltic tripotassium nitrite, is appreciably soluble in water, but nearly insoluble in KNO_2 solution; it is decomposed by HCl; hence the necessity for driving off the acid and evaporating to a few drops before adding the 50 c.c. KNO_2 solution.

120. A or B. The scheme in B is used whenever Cr is present; A is a shorter scheme which may be used to advantage when Cr is absent. When no precipitate is formed on the addition of NH_4OH to the original solution in the beginning, thus showing Fe, Al, and Cr absent, scheme A is used and much even of this scheme may be omitted. If the filtrate from the Co and Ni residue is very dilute, the solution may be colorless and still have Cr present. It is advisable, therefore, to evaporate 3 or 4 c.c. of the colorless solution nearly to dryness; if Cr is present, the solution will turn dark green.

121. Expel all the H_2S by boiling, otherwise it will be decomposed by HNO_3 in the subsequent boiling and troublesome free S will separate. H_2S is all gone when no odor of it arises from the boiling liquid, or better, when the vapors rising from the boiling liquid no longer blacken filter paper moistened with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Aq}$. If the solution bumps, put in a few pieces of glass tubing.

122. Convert ferrous Fe to ferric by boiling with HNO_3 because ferric hydrate is precipitated more satisfactorily than ferrous hydrate.

123. Boil off the excess of **free acid**, otherwise considerable NaOH will be needed to neutralize it, and impurities often contained in the NaOH will precipitate later where AlO_3H_3 is expected.

124. Add NaOH; this reagent should be perfectly clear and not too old. When a solution of sodium hydrate stands for any length of time, it absorbs silica from the glass of the bottle, and some of this impurity is likely to appear later in the test for Al.

125. The **extra 10 c.c. of NaOH** is to insure the solubility of the ZnO_2H_2 and AlO_3H_3 and their consequent separation from Fe and Mn.

126. The FeO_3H_3 and MnO_2H_2 precipitate may contain a little Co and Ni because any traces of CoS and NiS dissolved by HCl are precipitated as hydrates by NaOH along with the hydrates of Fe and Mn; these traces, however, do not affect the test for Fe and Mn.

127. Dilute the HCl solution of Fe with water before testing with $\text{K}_4\text{Fe}(\text{CN})_6$ because strong acid decomposes $\text{K}_4\text{Fe}(\text{CN})_6$ and the products of decomposition may react with the reagent to give the Fe test.

128. A dark blue precipitate with $\text{K}_4\text{Fe}(\text{CN})_6$ shows Fe present. From a Mn solution, $\text{K}_4\text{Fe}(\text{CN})_6$ precipitates white $\text{Mn}_2\text{Fe}(\text{CN})_6$, but this does not obscure the Fe test.

129. MnO_2H_2 fused with Na_2CO_3 on platinum foil produces Na_2MnO_4 , which has a characteristic green color. The presence of Fe does not obscure the green coloration. The test is very delicate, and care should be taken that the platinum foil is perfectly clean. The fused residue may easily be removed by boiling the foil in water. It is sometimes advisable to fuse a little Na_2CO_3 on the foil before adding the precipitate to be tested, to make sure no Mn is lurking in the folds of the foil.

130. Pass a very little H_2S into the Zn solution because an excess of H_2S changes the NaOH into NaSH, and this precipitates AlO_3H_3 , which resembles ZnS.

131. The ZnS precipitated by H_2S should be examined carefully; it should clot, and settle on standing. This distinguishes it from precipitated sulphur, which sometimes separates here and which is finely divided and does not clot. ZnS dissolves in dilute HCl, while S does not dissolve.

132. Add NH_4OH till alkaline for NH_4OH precipitates ZnO_2H_2 as well as AlO_3H_3 ; the former dissolves in slight excess of NH_4OH , but a large excess is necessary to dissolve the AlO_3H_3 .

133. A white and flocculent precipitate may not be Al at all; it may be gelatinous silicic acid which resembles AlO_3H_3 closely, and which got in as described in section 124. To distinguish between H_2SiO_3 and AlO_3H_3 fuse the precipitate on a Pt foil with KHSO_4 , or with K_2SO_4 moistened with a few drops of concentrated H_2SO_4 ; the H_2SiO_3 is decomposed, leaving insoluble SiO_2 , and the AlO_3H_3 is changed to $\text{Al}_2(\text{SO}_4)_3$; dissolve the fused mass in hot water, filter off the SiO_2 , and make slightly alkaline with NH_4OH ; a white flocculent precipitate indicates Al.

134. The test for Al is unsatisfactory at best, unless much Al is present. In case of doubt test for Al in the original solution if this is possible. If a metal is present that interferes with the test, remove it in such a manner that the conditions for precipitating Al shall be as favorable as possible. No definite directions can be given for this removal, as it depends entirely upon what metals are present with Al.

135. Neutralize free HNO_3 with $\text{Na}_2\text{CO}_3 + \text{Aq}$ to avoid using a large amount of BaCO_3 , because all the Ba put in here must be gotten rid of later. If too much Na_2CO_3 is added, so that a precipitate remains after shaking, add dilute HNO_3 drop by drop and shake till the precipitate dissolves. Na_2CO_3 precipitates all the metals that may be present here. Therein it acts differently from BaCO_3 , which throws down only Fe, Al, and Cr.

✓ **136.** BaCO_3 emulsion precipitates Fe, Al, and Cr as the hydrates. If the solution is cold, only these three come down; if it is hot, small amounts of the other metals may come down. The emulsion should be shaken before using. It is sometimes difficult to tell when enough BaCO_3 has been added on account of the gelatinous precipitate formed. If, after shaking, some white finely divided BaCO_3 settles to the bottom, BaCO_3 has probably been added in excess.

137. Dissolve the BaCO_3 in dilute HCl because BaCl_2 is insoluble in concentrated HCl .

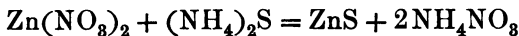
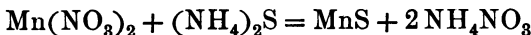
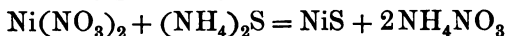
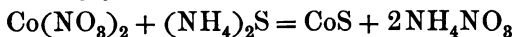
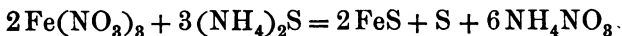
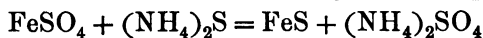
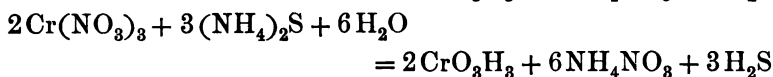
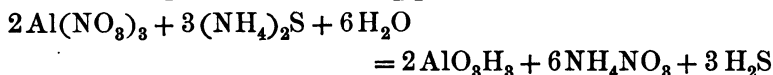
138. Heat to boiling because when BaSO_4 is precipitated hot it is more granular and does not run through the filter paper, as it often does when precipitated in the cold.

139. Boiling the NaOH solution of Cr precipitates CrO_3H_3 almost completely.

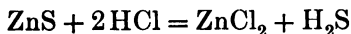
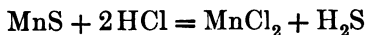
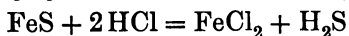
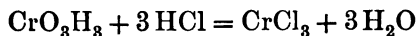
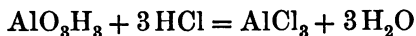
140. Short cuts in the analysis are allowable, of course, where the conditions warrant them. For instance, if the borax bead test on the residue supposed to contain Co and Ni shows both of these metals absent, subsequent treatment of that residue with aqua regia and KNO_3 may be omitted. Again, if in part B of the scheme the test with $\text{K}_4\text{Fe}(\text{CN})_6$ in (a) shows Fe absent, it is manifestly unnecessary to boil (b) with HNO_3 ; in that case it is sufficient to boil till the H_2S is expelled and then add Na_2CO_3 .

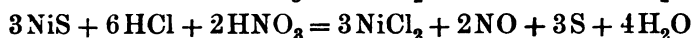
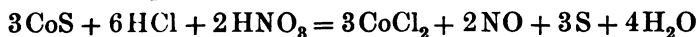
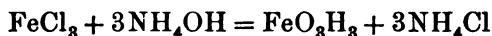
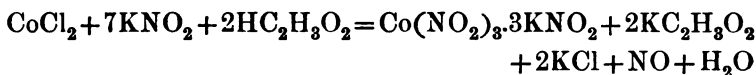
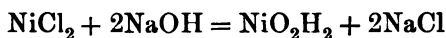
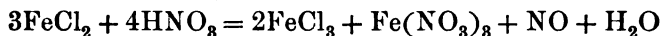
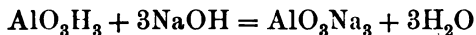
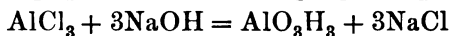
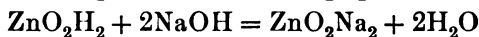
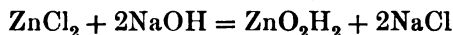
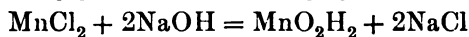
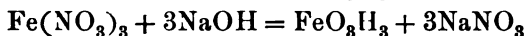
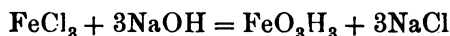
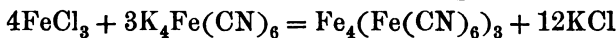
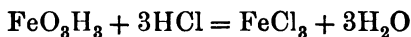
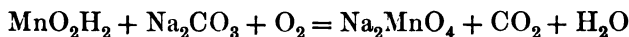
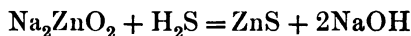
141. Equations for Scheme for Groups III and IV. — The following list contains the equations for all the reactions taking place in the analysis of a solution containing all the members of Groups III and IV.

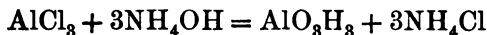
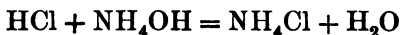
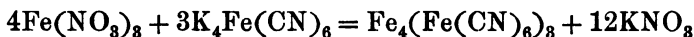
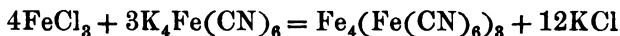
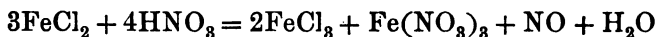
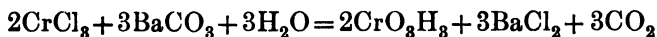
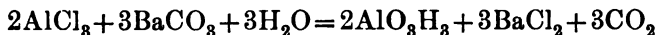
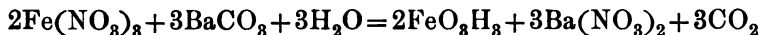
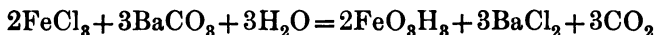
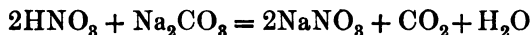
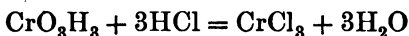
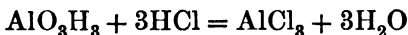
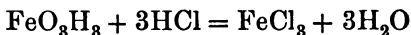
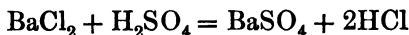
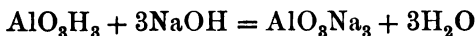
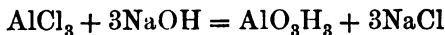
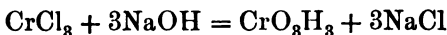
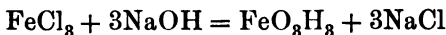
142. Precipitation with $(\text{NH}_4)_2\text{S}$.

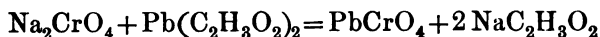
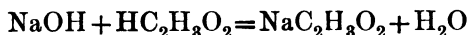
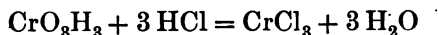
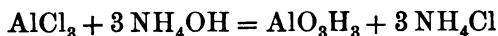
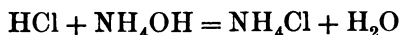
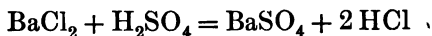
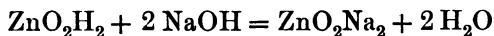
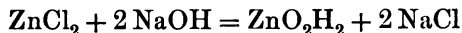
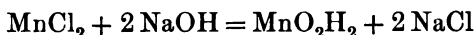
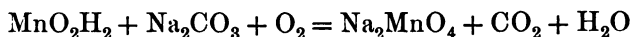
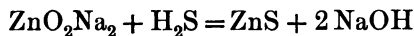


143. Treatment with HCl.



144. Dissolving CoS and NiS.**145. Removing Fe.****146. Test for Co.****147. Test for Ni.****148. Boiling with HNO₃.****149. Treatment with NaOH.****150. Test for Fe.****151. Test for Mn.****152. Test for Zn.**

153. Test for Al.**154. Test for Fe.****155. Treatment with Na_2CO_3 and BaCO_3 .****156. Dissolving in HCl.****157. Removing Ba.****158. Treatment with NaOH.**

159. Test for Cr.**160. Test for Al.****161. Removing Ba.****162. Treatment with NaOH.****163. Test for Mn.****164. Test for Zn.****GROUPS I, II, III, AND IV TOGETHER**

165. A solution containing Groups I, II, III, and IV together is analyzed in much the same way that solutions of the groups separately were analyzed. Groups III and IV are separated by means of the group reagent and the filtrate is examined for Groups I and II. The procedure for a solution containing the four groups may be found in the following scheme.

166. Scheme for Groups I, II, III, and IV

The solution contains Groups I, II, III, and IV. To 10 c.c. of the solution add NH_4Cl , NH_4OH ,^o and $(\text{NH}_4)_2\text{S}$, as in the scheme for Groups III and IV. Filter and save both precipitate and filtrate.

P. Contains AlO_3H_3 , CrO_3H_3 , FeS , CoS , NiS , MnS , and ZnS .

Proceed as with the corresponding precipitate in the **Scheme for Groups III and IV**. See sections **100**, **101**, and **102**.

F. Contains Groups I and II.^o Heat and add $(\text{NH}_4)_2\text{CO}_3$ in excess. Filter and save both precipitate and filtrate.

P. Contains BaCO_3 , SrCO_3 , and CaCO_3 .

Proceed as with the corresponding precipitate in the **Scheme for Group II**. See section **47**.

F. Contains **Mg** and **Group I**. Divide into (a) the smaller and (b) the larger portion.

Proceed as in the **Scheme for Groups I and II together**. See section **74**.

167. Notes on Scheme for Groups I, II, III, and IV together.

—The following notes will be of service in the analysis of a solution containing the four groups already studied; they refer mainly to the separation of Groups III and IV from Groups I and II; otherwise the work is exactly like that already done.

168. The NH_4OH added at the beginning should not be in excess, otherwise some **Al** if present might dissolve in the excess of NH_4OH . The **Al** would then run through into the **Group II** solution and appear as white flocculent AlPO_4 when the test for **Mg** is made with Na_2HPO_4 .

169. The filtrate which contains **Groups I and II** should be colorless or only light yellow. If it is black or brown, a little **NiS** has dissolved in the excess of $(\text{NH}_4)_2\text{S}$; acidifying the solution with HCl and boiling precipitates the **NiS**, which may then be filtered off. If the filtrate containing **Groups I and II** is pink, **Cr** has dissolved in excess of NH_4OH , and it may be precipitated as the hydrate by boiling the solution. If the filtrate containing **Groups I and II** has become turbid with precipitated **S** from standing in air, or if it becomes turbid when warmed, add HCl till acid, and boil five or ten minutes; then filter and add $(\text{NH}_4)_2\text{CO}_3$.

GROUP V. Ag, Pb, Hg, Cu, Cd, Bi

170. List of Members. — The members of Group V are:

Ag	Silver.
Pb	Lead.
Hg	Mercury.
Cu	Copper.
Cd	Cadmium.
Bi	Bismuth.

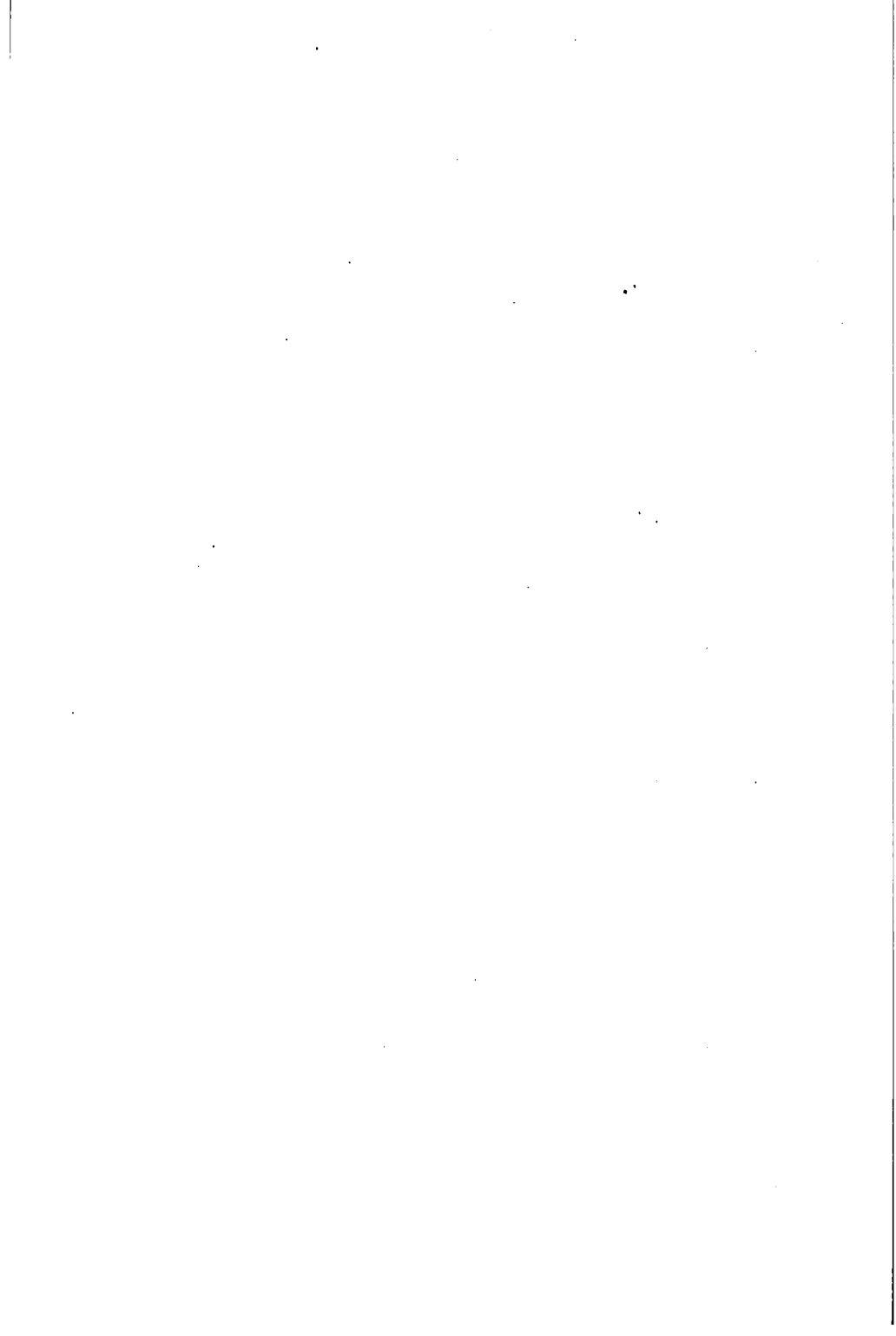
Two members of this group resemble iron in that they exist in two different states of oxidation; they are Cu and Hg; Cu forms both cuprous and cupric compounds, but the former oxidize easily in air and pass over into the corresponding cupric salts, so that the Cu salts commonly used are generally cupric salts; Hg forms both mercurous and mercuric compounds, and as they are all generally stable substances it becomes necessary to determine which state of Hg is present in the course of an analysis. For all practical purposes the other members of the group may be considered as forming compounds in only one state.

171. Preliminary Work. — Take in separate test tubes about 10 c.c. each of solutions of AgNO_3 , $\text{Pb}(\text{NO}_3)_2$, HgNO_3 (mercurous nitrate), HgCl_2 (mercuric chloride), $\text{Cu}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, and $\text{Bi}(\text{NO}_3)_3$. The HgNO_3 and $\text{Bi}(\text{NO}_3)_3$ solutions should be made up as directed in sections 411 and 412 respectively; the other solutions should have a strength of 1:40. To each solution add a little dilute HCl ; note in which cases a precipitate is formed; when a precipitate is formed, determine its solubility in hot water, also in NH_4OH . To separate portions of solutions of the members of the group add NH_4OH , first in small quantities to see if a precipitate forms, then in excess to see if any of the precipitates dissolve. Then take again separate portions of the same original solutions and pass in a little H_2S , and try the solubility of the resulting sulphides in dilute HNO_3 , first cold, then hot. Finally dilute small portions of the solutions with large amounts of water by pouring

Reagent	Silver $\text{AgNO}_3 + \text{Aq}$	Lead $\text{Pb(NO}_3)_2 + \text{Aq}$	Mercurous Mercury $\text{HgNO}_3 + \text{Aq}$	
Dil. HCl.	White ppt., AgCl ; insol. in hot water; sol. in NH_4OH from which dil. HNO_3 reppts. AgCl .	White ppt., PbCl_2 ; sol. in hot water from which dil. H_2SO_4 ppts. PbSO_4 ; PbCl_2 is insol. in NH_4OH .	White ppt., HgCl ; insol. in hot water; NH_4OH turns it black, probably a mix- ture of HgNH_2Cl and Hg.	1
NH_4OH .	Brown ppt., Ag_2O ; sol. in ex- cess; sol. in dil. HNO_3 .	White basic ppt.; sol. in dil. HNO_3 .	Black ppt. of complicated com- position; insol. in dil. HNO_3 .	E in
H_2S .	Black ppt., Ag_2S ; insol. in cold, sol. in hot, dil. HNO_3 .	Black ppt., PbS ; insol. in cold, sol. in hot, dil. HNO_3 .	Black ppt., HgS (and Hg); insol. in cold and in hot dil. HNO_3 ; turns white when boiled.	n lc b ir di sa
Dilute with H_2O .	No ppt.	No ppt.	No ppt.	

Primary Work for Group V

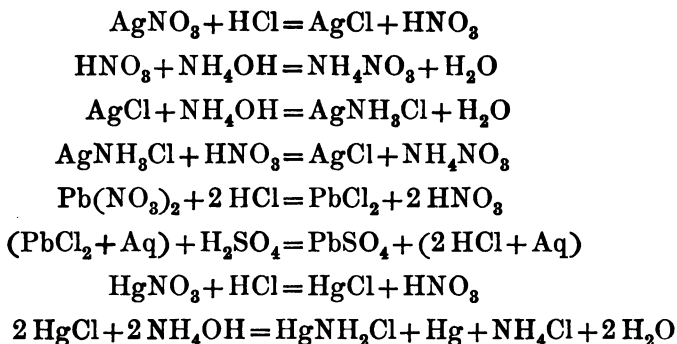
Mercuric Mercury $\text{HgCl}_2 + \text{Aq}$	Copper $\text{Cu}(\text{NO}_3)_2 + \text{Aq}$	Cadmium $\text{Cd}(\text{NO}_3)_2 + \text{Aq}$	Bismuth $\text{Bi}(\text{NO}_3)_3 + \text{Aq}$
No ppt.	No ppt.	No ppt.	No ppt.
White ppt., HgNH_2Cl ; insol. in dil. HNO_3 .	Greenish blue, basic ppt.; sol. in excess to dark blue solution; sol. in dil. HNO_3 .	White ppt., CdO_2H_2 ; sol. in large excess; sol. in dil. HNO_3 .	White ppt., BiO_2H_3 ; partly sol. in dil. HNO_3 .
White ppt., run- ning through yel- low, red-brown to black HgS ; insol. in cold and in hot dil. HNO_3 ; sol. in aqua regia.	Black ppt., CuS ; insol. in cold, sol. in hot, dil. HNO_3 .	Yellow ppt., CdS ; insol. in cold, sol. in hot, dil. HNO_3 .	Brownish-black ppt., Bi_2S_3 ; insol. in cold, sol. in hot, dil. HNO_3 .
No ppt.	No ppt.	No ppt.	White basic ppt., $\text{BiNO}_3(\text{OH})_2$.



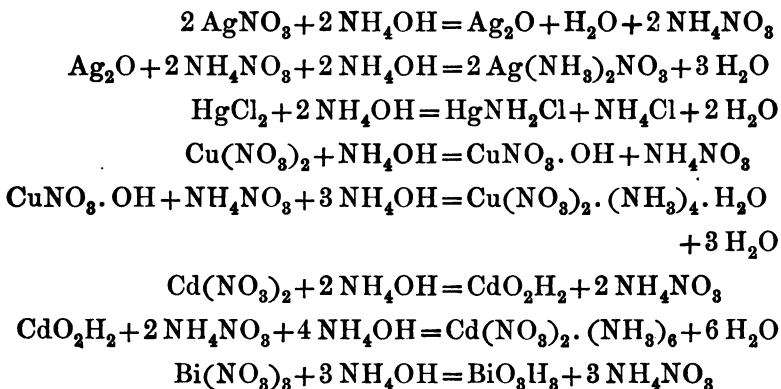
a few drops of each solution into a test tube of water, and note the tendency of Bi to form insoluble basic salts. Incidentally, if the details of the Groups III and IV work have caused you to forget for the moment the necessity of seeing results just as they are, read section 37 again. Verify all the results in the following table.

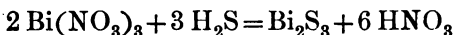
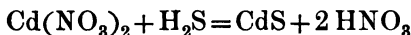
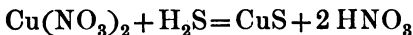
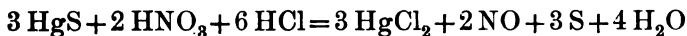
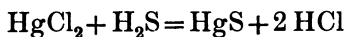
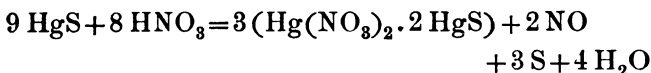
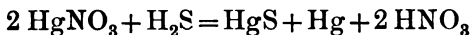
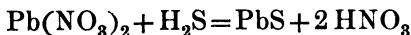
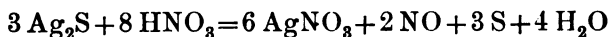
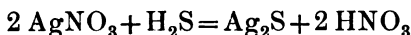
173. Equations for Preliminary Work for Group V. — The following list contains the equations for all the reactions taking place in the preliminary work for Group V indicated in the preceding table.

174. Chlorides.



175. Hydrates.



176. Sulphides.**177. Action with H_2O .**

178. The Known Solution on Group V. — Since mercuric chloride is the most convenient mercuric salt to use, and since salts of Ag, Pb, and mercurous Hg cannot be present in a solution containing a chloride, it will be necessary to divide the analysis of the known solution on Group V into two parts. First analyze a solution containing Ag, Pb, and mercurous Hg; then examine another solution containing mercuric Hg, Pb (trace), Cu, Cd, and Bi. Use the proper parts of the following scheme in the analysis of these solutions. As in the case of previous known solutions, do the work thoughtfully and write up a full account of it in the notebook.

1. The first part of the report discusses the importance of maintaining accurate records of all transactions, including sales, purchases, and expenses. It emphasizes the need for a systematic approach to record-keeping, such as using a ledger or accounting software, to ensure that all data is properly documented and organized.

2. The second part of the report focuses on the importance of regular reconciliation of accounts. This involves comparing the company's internal records with external statements, such as bank statements or supplier invoices, to identify any discrepancies and correct them promptly. This process helps to prevent errors and ensures that the company's financial statements are accurate and reliable.

3. The third part of the report discusses the importance of maintaining a clear and concise record of all transactions. This includes using a consistent format for recording data, such as using a standard set of codes or abbreviations, and ensuring that all entries are clearly labeled and dated. This makes it easier to review and analyze the data, and helps to prevent confusion or misinterpretation.

4. The fourth part of the report discusses the importance of maintaining a secure and confidential record of all transactions. This involves implementing appropriate security measures, such as password protection and access controls, to ensure that the data is protected from unauthorized access or theft. It also emphasizes the need for proper disposal of records when they are no longer needed, to prevent the release of sensitive information.

5. The fifth part of the report discusses the importance of maintaining a clear and concise record of all transactions. This includes using a consistent format for recording data, such as using a standard set of codes or abbreviations, and ensuring that all entries are clearly labeled and dated. This makes it easier to review and analyze the data, and helps to prevent confusion or misinterpretation.

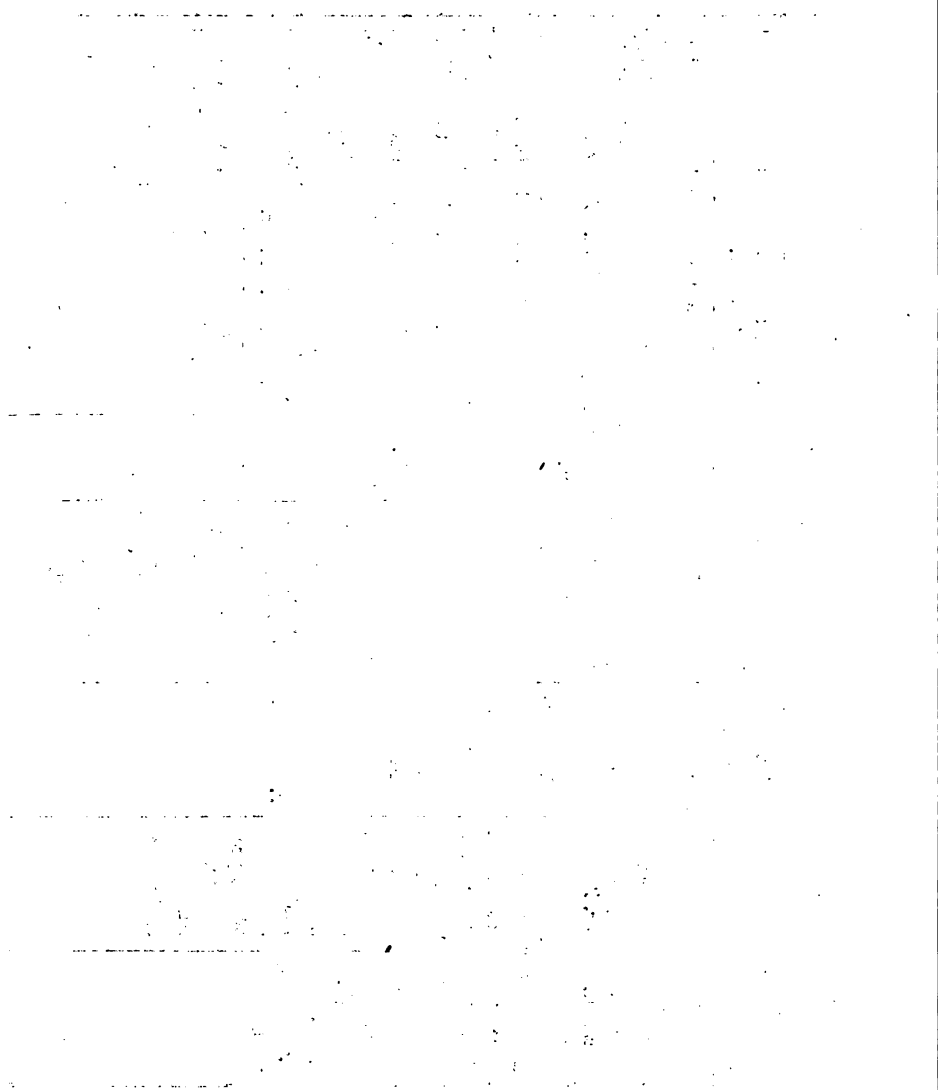
6. The sixth part of the report discusses the importance of maintaining a secure and confidential record of all transactions. This involves implementing appropriate security measures, such as password protection and access controls, to ensure that the data is protected from unauthorized access or theft. It also emphasizes the need for proper disposal of records when they are no longer needed, to prevent the release of sensitive information.

7. The seventh part of the report discusses the importance of maintaining a clear and concise record of all transactions. This includes using a consistent format for recording data, such as using a standard set of codes or abbreviations, and ensuring that all entries are clearly labeled and dated. This makes it easier to review and analyze the data, and helps to prevent confusion or misinterpretation.

8. The eighth part of the report discusses the importance of maintaining a secure and confidential record of all transactions. This involves implementing appropriate security measures, such as password protection and access controls, to ensure that the data is protected from unauthorized access or theft. It also emphasizes the need for proper disposal of records when they are no longer needed, to prevent the release of sensitive information.

9. The ninth part of the report discusses the importance of maintaining a clear and concise record of all transactions. This includes using a consistent format for recording data, such as using a standard set of codes or abbreviations, and ensuring that all entries are clearly labeled and dated. This makes it easier to review and analyze the data, and helps to prevent confusion or misinterpretation.

10. The tenth part of the report discusses the importance of maintaining a secure and confidential record of all transactions. This involves implementing appropriate security measures, such as password protection and access controls, to ensure that the data is protected from unauthorized access or theft. It also emphasizes the need for proper disposal of records when they are no longer needed, to prevent the release of sensitive information.



180. Notes on Scheme for Group V. — The following notes will be found of service in the analysis of a solution for Group V; they cover ground similar to that covered by the notes on preceding groups.

181. The solution may contain any possible combination of AgNO_3 , $\text{Pb(NO}_3)_2$, HgNO_3 , HgCl_2 , $\text{Cu(NO}_3)_2$, $\text{Cd(NO}_3)_2$, and $\text{Bi(NO}_3)_3$; but it may contain mercuric Hg only in the absence of Ag, Pb, and mercurous Hg.

182. If dilute HCl in slight excess causes no precipitate, it shows Ag and mercurous Hg absent. It does not prove that Pb is absent, however, for PbCl_2 is partly soluble in water, and the Pb may not come down if the solution is dilute or hot; in such a case it will appear later as PbS. Occasionally dilute HCl may cause a white precipitate that dissolves when more HCl is added; this is BiOCl , insoluble in water, but soluble in excess of HCl.

183. The slight excess of HCl may be determined in the same way that the excess of $(\text{NH}_4)_2\text{CO}_3$ was determined in Group II. A large excess of HCl should be avoided, however, as it interferes with the precipitation of the rest of the group with H_2S .

184. Shake gently the precipitate caused by HCl in order to render it granular so that it will settle well. Too much shaking causes the AgCl to form in large clots, which are likely to inclose considerable quantities of the original solution and prevent the HCl from reacting therewith.

185. Wash once with cold water in order to free the precipitate from the solution containing the other members of the group.

186. Add water and bring to a boil in order to insure complete solution of the PbCl_2 . If the 10 c.c. of solution started with contained only $\text{Pb(NO}_3)_2$ of a strength of 1:10, then 50 c.c. of water would be needed to dissolve the PbCl_2 completely. Generally a smaller amount will suffice. In special cases where a much stronger solution of a Pb salt is used more water must, of course, be added, but this greater strength will generally be indicated by a very copious precipitate with HCl.

187. Wash the residue containing AgCl and HgCl once with hot water to remove completely the PbCl_2 , otherwise the NH_4OH will form a white basic salt which passes through the filter and gives a turbid filtrate which becomes clear, however, when HNO_3 is added.

188. Add NH_4OH ; this dissolves AgCl , forming a double salt, AgNH_2Cl , which is soluble in water and in NH_4OH , but which is broken down when HNO_3 is added, with consequent reprecipitation of AgCl .

189. Verify Pb by adding H_2SO_4 to the solution containing PbCl_2 . A more reliable test is to pass in a little H_2S and get black PbS , but the H_2SO_4 test is more convenient and answers well if Group V only is present. Cases where the H_2S test is necessary will be considered later where such cases arise.

190. Pb pres.; this metal appears in two places in the scheme because it is seldom separated completely from the other members of the group by HCl . From strong solutions of Pb salts HCl will sometimes precipitate the Pb completely; more often the acid will separate the most of it as PbCl_2 and leave a little in the filtrate to be removed by H_2SO_4 later; from dilute or hot solutions of Pb salts HCl may fail to precipitate any PbCl_2 . In that case all the Pb will appear in the second place in the scheme.

191. Precipitation with H_2S should be done with great care. The presence of a little HCl does no harm, but a large excess should be avoided, for it prevents complete precipitation. The solution should be hot, but not actually boiling. It is well to let the mixture stand a few minutes before testing by odor for excess of H_2S .

192. If H_2S causes a precipitate that dissolves immediately on shaking, it shows that free HNO_3 is probably present. H_2S must then be passed in till the free HNO_3 is all decomposed; or better, the original excess of HNO_3 may be diminished by boiling before passing in the H_2S . Much free HNO_3 in the original solution indicates the probable presence of Bi salts, which tend to form insoluble basic salts with water, but which are readily soluble in the acid.

193. Complete precipitation by H_2S may be assured in case of doubt by taking a little of the filtrate from the H_2S precipitate, diluting it with several times its volume of water, and passing in more H_2S . Adding water dilutes the strong acid which by its presence in the original solution may have prevented complete precipitation of the sulphides.

194. The color of the precipitate caused by H_2S is generally black unless Cd alone is present, when it is yellow. From solutions of

halogen salts of cadmium, H_2S produces a precipitate which is deep orange at first, but which turns lighter as more H_2S is passed in. If a precipitate is obtained that is white at first but changes through yellow and red to black, mercuric Hg is probably present. If much HCl is present, Pb may come down as an orange-red precipitate which is decomposed by excess of H_2S to black PbS. Precipitated S may appear if much acid was present in the solution. All other legitimate precipitates here are black.

195. Boiling with dilute HNO_3 dissolves the sulphides of Pb, Cu, Cd, and Bi. HgS remains insoluble and black, though continued boiling may change it to white insoluble $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgS}$. The confirmatory test for Hg with SnCl_2 must therefore be applied, no matter what the color of the residue may be.

196. A black residue after boiling with HNO_3 is probably HgS , but it may be only precipitated S which has clotted and inclosed PbS, CuS, or Bi_2S_3 . A black residue does not indicate Hg conclusively, and the SnCl_2 test must be applied.

197. Hot HCl and KClO_3 give nascent Cl, which changes the rather insoluble HgS to HgCl_2 . The reaction is thought to be: $2\text{KClO}_3 + 4\text{HCl} = 2\text{KCl} + 2\text{Cl} + 2\text{ClO}_2 + 2\text{H}_2\text{O}$. The solution of HgS in HCl is accomplished conveniently by heating a few c.c. of concentrated HCl in a test tube, adding a crystal of KClO_3 , and pouring the hot mixture on the HgS in the filter paper. If one treatment does not effect solution, heat the filtrate, and pour it again upon the filter. Compare this with the solution of CoS and NiS in aqua regia in section 117.

198. The stannous chloride, $\text{SnCl}_2 + \text{Aq}$, must be fresh; if it has run over into stannic chloride, SnCl_4 , no precipitate will be formed, even though Hg be present.

199. Boiling till white fumes of H_2SO_4 appear insures the complete expulsion of HNO_3 , in which PbSO_4 is somewhat soluble. The resulting liquid is diluted with water because PbSO_4 is somewhat soluble in concentrated H_2SO_4 , but nearly insoluble in dilute H_2SO_4 . To separate Pb completely needs considerable care. Therefore the precautions should be observed closely.

200. Add NH_4OH ; the precipitate caused by NH_4OH is not necessarily BiO_3H_3 , for if Pb has not been removed completely by H_2SO_4 , it will be precipitated here as white PbO_2H_2 ; hence the necessity of trying the confirmatory test for Bi.

201. The confirmatory test for Bi is delicate only when all the HCl has been removed by boiling. The presence of HCl may prevent entirely the precipitation of BiOCl.

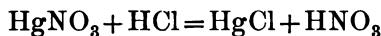
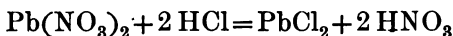
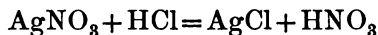
202. If the solution is blue, this is test enough for the presence of Cu. The $K_4Fe(CN)_6$ test need be applied only if the solution is colorless or nearly so.

203. $K_4Fe(CN)_6$ precipitates $Cu_2Fe(CN)_6$, which is red-brown. This is an extremely delicate test for Cu and should always be used if the solution is not blue. The $Cu_2Fe(CN)_6$ is not obscured by the white $Cd_2Fe(CN)_6$ which $K_4Fe(CN)_6$ precipitates from Cd solutions.

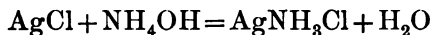
204. KCN solution forms with Cd the double salt $Cd(CN)_2 \cdot 2 KCN$ which is soluble in water and from whose solution H_2S precipitates the yellow CdS. KCN solution forms with Cu a colorless solution containing CuCN $\cdot 3 KCN$ from which H_2S cannot precipitate the Cu.

205. Equations for Scheme for Group V.—The following list contains the equations for all the reactions taking place in the analysis of a solution containing the six members of Group V.

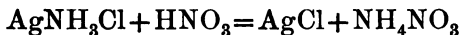
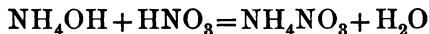
206. Precipitation with HCl.



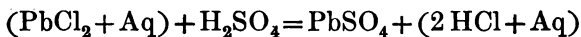
207. Treatment with NH_4OH .

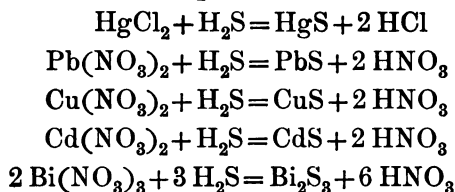
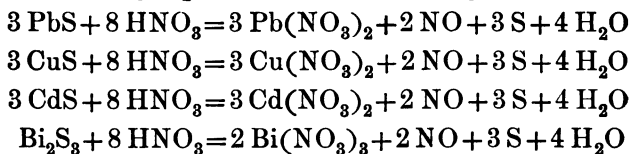
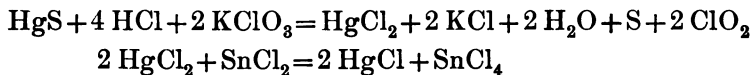
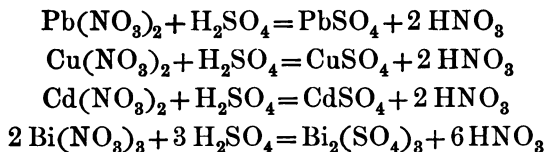
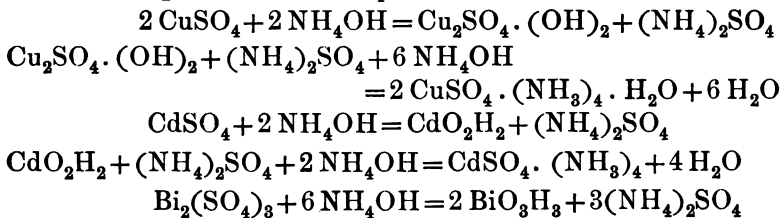
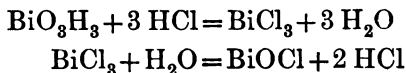


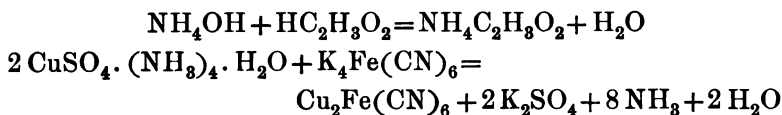
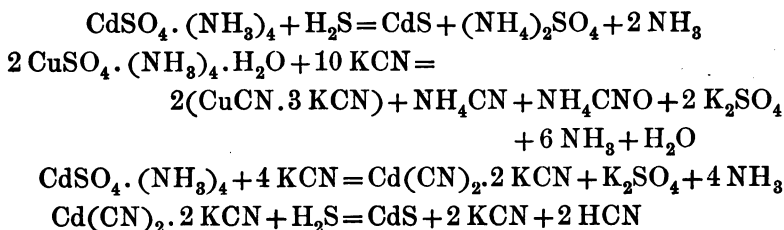
208. Test for Ag.



209. Test for Pb.



210. Precipitation with H_2S .**211.** Dissolving H_2S precipitates in HNO_3 .**212.** Dissolving HgS and test for Hg .**213.** Treatment with H_2SO_4 .**214.** Precipitation with NH_4OH .**215.** Test for Bi .

216. Test for Cu.**217. Test for Cd.****GROUPS I, II, III, IV, AND V TOGETHER**

218. A solution containing Groups I, II, III, IV, and V together is analyzed in much the same way that a solution containing Groups I, II, III, and IV was analyzed, except that Group V is eliminated first by means of its group reagents HCl and H₂S; the filtrate is then treated exactly like a solution containing Groups I to IV. The procedure for a solution containing the first five groups may be found in the following scheme. By the time the student has reached this stage of the year's work he should be so familiar with the schemes for the separate groups of bases that the following scheme for a solution containing all the members of the first five groups of bases will be needed only to cover the points of difficulty or newness incident to the separation of the groups from each other. As soon as each group-precipitate has been separated by itself, the student should be able to proceed with the examination of this precipitate without having to turn back to the scheme for that particular group. It will be noted, of course, that these schemes for combinations of groups of bases are not entirely new schemes; each simply adds a little to the next preceding scheme for several groups together.

219. Scheme for Groups I, II, III, IV, and V

To the solution containing Groups I, II, III, IV, and V add cold dilute HCl° till no more precipitate is formed. Filter, and save both precipitate and filtrate.

P. Contains AgCl , PbCl_2 , HgCl .

Proceed as with the corresponding precipitate in the **Scheme for Group V**. See section **179**.

F. Contains the rest of Group V and all of Groups I, II, III, and IV. Transfer to a flask and pass H_2S° into the hot, slightly acid solution with constant shaking till the odor of H_2S is distinctly perceptible after standing a few minutes. Filter, and save both precipitate and filtrate.^o

P. Contains HgS , PbS , CuS , CdS , and Bi_2S_3 .

Proceed as with the corresponding precipitate in the **Scheme for Group V**. See section **179**.

F. Contains Groups I, II, III, and IV. Warm in a flask and add NH_4Cl , $\text{NH}_4\text{OH}^\circ$ till alkaline, and then $(\text{NH}_4)_2\text{S}$. Filter, and save both precipitate and filtrate.

P. Contains AlO_3H_3 , CrO_3H_3 , FeS , CoS , NiS , MnS and ZnS .

Proceed as with the corresponding precipitate in the **Scheme for Groups III and IV**. See sections **100**, **101**, and **102**.

F. Contains Groups I and II. Heat and add $(\text{NH}_4)_2\text{CO}_3$ in excess. Filter, and save both precipitate and filtrate.

P. Contains BaCO_3 , SrCO_3 , CaCO_3 . Proceed as with the corresponding precipitate in the **Scheme for Group II**. See section **47**.

F. Contains Mg and Group I. Divide into (a) the smaller and (b) the larger portion. Proceed as in the **Scheme for Groups I and II**. See section **74**.

220. Notes on Scheme for Groups I, II, III, IV, and V together.

— The following notes will be of service in the analysis of a solution containing all the five groups already studied ; they refer mainly to the separation of Group V from the other four groups ; only a few notes are added, as all the notes on the preceding schemes hold good here, and the student should refer to these

notes in case of doubt — or better still, he should have all the preceding work so well in mind that he need not refer back to work already done.

221. Use cold dilute HCl to precipitate AgCl, PbCl₂, and HgCl; if concentrated HCl were used, certain salts soluble in water but less soluble in concentrated HCl might be precipitated; the salt most likely to do this is BaCl₂, and it might easily be mistaken for PbCl₂, as it dissolves in water and gives a white precipitate when H₂SO₄ is added to its solution. When cold dilute HCl is added to the original solution, a fine white precipitate may come down which is not AgCl, PbCl₂, or HgCl, but an oxychloride of Bi; this BiOCl is produced on account of the dilution of the original solution by the water of the dilute HCl. This oxychloride is soluble in an excess of HCl.

222. Before beginning to pass H₂S into the solution it is well to test it with litmus paper. If the solution contains much free HNO₃ or concentrated HCl, the H₂S will be decomposed with the separation of S, and sometimes with the evolution of NO₂ fumes. If the solution is strongly acid, it should be evaporated nearly to dryness and the residue dissolved in water, with the addition of a few drops of HCl if necessary; then pass in H₂S; wash the precipitated sulphides well to get rid of any occluded solution of Groups III and IV metals, particularly Fe and Al; if these are not washed out, their hydrates will appear when NH₄OH is added for the Bi test later.

223. Have hot but not boiling the solution into which H₂S is passed, because a boiling acid solution is apt to dissolve the sulphides precipitated here.

224. The filtrate from the precipitated sulphides of Group V contains Groups I to IV, but it may also contain small amounts of Pb and Cd, if the solution was too strongly acid before passing in the H₂S. It is advisable, therefore, to dilute a little of this filtrate with water and pass in some more H₂S; if no precipitate forms, all is well; if a precipitate does form, the rest of the filtrate should be treated the same way, because any member of Group V not entirely removed by H₂S is likely to appear in Group IV work and confuse the tests there.

225. If NH_4OH produces a black precipitate when it is added to the filtrate containing Groups I, II, III, and IV, it shows that the filtrate contained some H_2S and this reacted with the NH_4OH , forming $(\text{NH}_4)_2\text{S}$, which precipitated some CoS , NiS , and FeS . Occasionally the addition of NH_4OH to a solution containing H_2S causes a dark or black coloration but no precipitate; this coloration may be neglected.

226. Review the two notes on the Scheme for Groups I, II, III, and IV together; both notes apply here.

GROUP VI. As, Sb, Sn

227. List of Members. — The members of Group VI are :

As	Arsenic.
Sb	Antimony.
Sn	Tin.

All three members exist in two states of oxidation ; not all the six states are of sufficient importance to be considered here ; of the first two members only arsenous As and antimonous Sb will be considered ; both stannous and stannic Sn must be taken up, however.

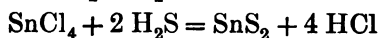
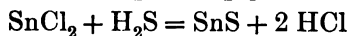
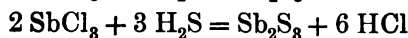
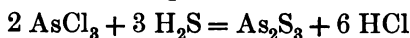
228. Preliminary Work. — Take in separate test tubes about 10 c.c. each of solutions of AsCl_3 (arsenous chloride), SbCl_3 (antimonous chloride), SnCl_2 (stannous chloride), and SnCl_4 (stannic chloride). These solutions may all have a strength of 1 : 40. To each add a little dilute HCl . Into fresh portions pass H_2S ; note the colors of the precipitates ; then proceed as follows : Filter the As_2S_3 ; break a hole in the point of the filter and, by means of the wash bottle, wash the As_2S_3 into a large test tube, using perhaps 40 c.c. of water ; shake till the arsenous sulphide precipitate is well suspended in the water and then divide the emulsion into four parts ; test the first part with cold dilute HCl , the second with hot concentrated HCl , the third with yellow ammonium sulphide, and the fourth with concentrated ammonium carbonate solution ; verify all the solubilities for As_2S_3 given in the following table ; study the other

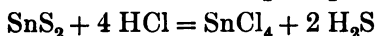
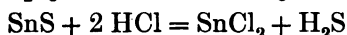
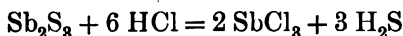
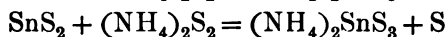
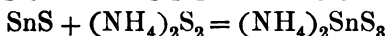
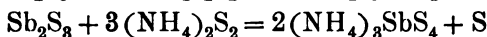
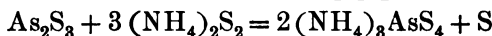
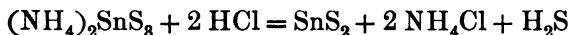
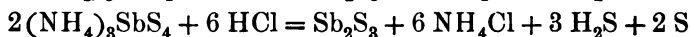
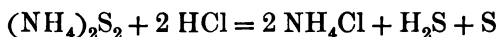
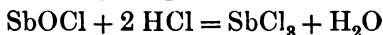
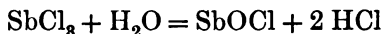
three precipitated sulphides in the same way. Finally dilute fresh portions of the original solutions with water.

229. Table of Preliminary Work for Group VI				
Reagent	Arsenic (ous) AsCl ₃ + Aq	Antimony (ous) SbCl ₃ + Aq	Tin (stannous) SnCl ₂ + Aq	Tin (stannic) SnCl ₄ + Aq
HCl.	No ppt.	No ppt.	No ppt.	No ppt.
H ₂ S.	Yellow ppt., As ₂ S ₃ , arsenous sulphide. Insol. in dil. HCl. Insol. in cold conc. HCl., partly sol. in hot. Sol. in yellow (NH ₄) ₂ S ₂ . HCl reppts. As ₂ S ₃ . Sol. in conc. (NH ₄) ₂ CO ₃ + Aq. HCl reppts. As ₂ S ₃ .	Orange ppt., Sb ₂ S ₃ , antimo- nous sulphide. Insol. in dil. HCl. Sol. in cold conc. HCl. Sol. in yellow (NH ₄) ₂ S ₂ . HCl reppts. Sb ₂ S ₃ . Insol. in conc. (NH ₄) ₂ CO ₃ + Aq.	Dark brown ppt., SnS, stan- nous sulphide. Insol. in dil. HCl. Sol. in cold conc. HCl. Sol. in yellow (NH ₄) ₂ S ₂ . HCl reppts. SnS ₂ . Insol. in conc. (NH ₄) ₂ CO ₃ + Aq.	Yellow ppt., SnS ₂ , stannic sulphide. Insol. in dil. HCl. Partly sol. in cold conc. HCl, easily in hot. Sol. in yellow (NH ₄) ₂ S ₂ . HCl reppts. SnS ₂ . Insol. in conc. (NH ₄) ₂ CO ₃ + Aq.
Dilute with water.	No ppt.	White ppt., SbOCl. Sol. in HCl.	No ppt.	No ppt.

230. Equations for Preliminary Work for Group VI. — The following list contains the equations for all the reactions taking place in the preliminary work for Group VI in the preceding table.

231. Precipitation of sulphides.



232. Solution of sulphides in HCl.**233.** Solution of sulphides in $(\text{NH}_4)_2\text{S}_2$.**234.** Reprecipitation of sulphides by HCl.**235.** Side reaction.**236.** Dilution of Sb solution.

237. The Known Solution on Group VI. — Analyze a known solution containing As, Sb, and Sn, and write up a detailed account of the work as in the case of previous known solutions. The complete separation of As, Sb, and Sn is at best very unsatisfactory, principally because there is no reagent which will dissolve one member completely without dissolving a little of the other at the same time. The ability to go through the known solution according to the scheme and get every result sharply and accurately will facilitate greatly the examination of unknown solutions. This is particularly true in this group. Special attention should be given the reagents to see that they are in proper condition.

238.		Scheme for Group VI	
<p>Put 10 c.c. of a solution° containing As, Sb, and Sn in a flask or beaker ; warm, and pass in H₂S° with shaking till there is a distinct odor of H₂S after shaking. Filter.</p>			
<p>P. Contains As₂S₃,° Sb₂S₃, SnS, and SnS₂. Tear off that part of the filter paper containing the precipitate, put it in a small beaker, add a little concentrated HCl, and heat gently but do not boil.° Then dilute with a little water, filter, and wash the undissolved residue.°</p>			
<p>Residue contains As₂S₃ and traces of Sb and Sn.° Dissolve it on the filter paper in a little concentrated HCl to which a crystal of KClO₃° has been added. Boil off the excess of chlorine.° Add NH₄OH till alkaline. Filter.</p>		<p>F. Contains SbCl₃ and SnCl₄, with a small amount of H₃AsO₄.° Set up a generator consisting of a flask, thistle tube, and delivery tube ; to the latter attach a glass tube containing dry CaCl₂, and to this a hard glass tube drawn down to a capillary. Put some zinc and a piece of platinum foil in the flask, and add dilute HCl. When the air has all been expelled from the apparatus, light the hydrogen issuing from the capillary, <i>using the safety tube</i>.° Heat the hard glass tube just back of the capillary for a few minutes, and if no mirror is formed, add the filtrate containing Sb and Sn a little at a time. Continue heating the hard glass tube while the gases pass through, and look for a deposit in the capillary tube.</p>	
<p>P. SbO₃H₃ and SnO₄H₄. Reject.</p>	<p>F. Contains AsCl₃ and a little NH₄OH. Add some more NH₄OH, say about half as much by volume as you had filtrate. Add a little NH₄Cl and then some MgCl₂. If no precipitate forms immediately, stir the mixture and let it stand several hours.° White precipitate, MgNH₄AsO₄.° ∴ As pres.°</p>	<p>Residue in the flask consists of zinc on which the Sn has deposited and the platinum foil on which part of the Sb has deposited as a black coating. Pour the contents of the flask into a beaker, and wash the residue by decantation with water. Add concentrated HCl and heat till the residue has all dissolved. Dilute with water and add HgCl₂. White precipitate, HgCl. ∴ Sn pres.</p>	
		<p>Gas evolved contains SbH₃ and traces of AsH₃. These are broken down by heat and the Sb and As are deposited in the capillary. Break off that part of the glass tube containing the mirror° and drop it into some NaOCl solution in a test tube.</p>	
		<p>If the mirror dissolves readily, the gas contained only AsH₃.</p>	<p>If the mirror does not dissolve readily, it shows Sb pres.</p>

239. Notes on Scheme for Group VI. — The following notes will be found of service in the analysis of a solution for Group VI; they cover ground similar to that covered by the notes on preceding groups.

240. The original solution should contain enough free HCl to keep the As, Sb, and Sn in solution. A large excess of acid should be avoided, because that prevents complete precipitation of Sb and Sn. If the original solution is strong of HCl, it should be diluted with water before passing in H_2S . This diluting may throw out white insoluble $SbOCl$, but it is not necessary to add more HCl to dissolve this, as it is readily converted to Sb_2S_3 by H_2S .

241. When H_2S is passed into a solution containing As, Sb, and Sn, the sulphides often tend to assume the colloidal state, *i.e.* a yellowish, turbid liquid that leaves little or no residue on the filter paper when the solution is filtered. The addition of a few drops of HCl, or better some salt like $NH_4Cl + Aq$ or $BaCl_2 + Aq$, will cause the colloidal precipitate to drop out in the usual form of precipitate.

242. As_2S_3 comes down very slowly in the cold if the As is present as an arsenate. Heating hastens the action a little, but even then the liquid should be kept nearly boiling while the H_2S is passed in, and the resulting solution saturated with H_2S should be allowed to stand awhile. A slow yellow precipitate under such conditions strongly indicates As.

243. Heat gently, but do not boil, because boiling with HCl dissolves considerable of the As_2S_3 .

244. The undissolved residue consists of shreds of filter paper mixed with undissolved As_2S_3 ; subsequent treatment with nascent chlorine dissolves the sulphide and leaves the filter paper shreds unchanged.

245. Traces of Sb and Sn are often found in the residue of As_2S_3 on account of the difficulty of dissolving Sb_2S_3 , SnS , and SnS_2 in concentrated HCl without having considerable quantities of As go into solution at the same time.

246. Hot HCl and $KClO_3$ give nascent chlorine. Use the same method employed when dissolving HgS in HCl and $KClO_3$. See section 197.

247. Be sure to boil off the excess of chlorine, because its presence interferes with the test for As. The absence of the odor of chlorine

shows when the solution has been boiled enough. The odor of HCl may be present if the acid also has not been boiled off, but the presence of a little HCl does no harm; a large excess of it, however, should be avoided, as all the excess must be neutralized later with NH_4OH .

248. Let stand several hours; if after twelve hours no precipitate has formed, As may be considered absent.

249. The $\text{MgNH}_4\text{AsO}_4$ test, like the MgNH_4PO_4 test, is very delicate. The solution to which the MgCl_2 is added should be concentrated and should contain an excess of NH_4OH , because $\text{MgNH}_4\text{AsO}_4$ is somewhat soluble in water, but less soluble in NH_4OH . The precipitate is crystalline and sticks to the sides of the test tube, especially where they have been rubbed with the glass rod.

250. As present. A solution containing As alone is more easily tested as follows: Treat the precipitated sulphides with concentrated $(\text{NH}_4)_2\text{CO}_3$ solution; As_2S_3 dissolves easily while Sb_2S_3 , SnS , and SnS_2 are insoluble; the addition of HCl reprecipitates the As_2S_3 from the $(\text{NH}_4)_2\text{CO}_3$ solution.

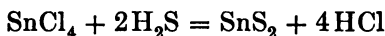
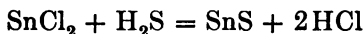
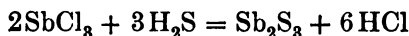
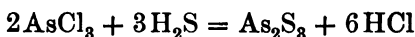
251. The H_3AsO_4 is formed by the action of HCl on As_2S_3 , and it is reduced by nascent hydrogen to AsH_3 without precipitation of As.

252. The safety tube method of lighting hydrogen is the only method that eliminates danger of explosion. It is applied as follows: Fill a small test tube with hydrogen as it issues from the capillary, and touch the mouth of the test tube to a Bunsen flame a few feet away from the apparatus. When the hydrogen is pure enough to burn in the test tube with a blue flame, carry it back to the capillary and light the stream of hydrogen with the flame in the test tube.

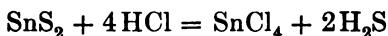
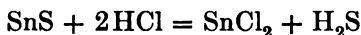
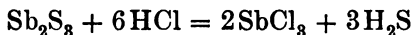
253. The mirror in the capillary is pretty sure to contain As if this metal is present in the original solution. The amount of As in the mirror depends on the amount of As_2S_3 that dissolved in the concentrated HCl; sometimes it is so large as to obscure the Sb mirror. Therefore a mirror must not be considered proof of the presence of Sb unless the platinum is distinctly blackened at the same time. It is sometimes possible to distinguish by the eye alone between the mirrors of As and of Sb, for that of As is blacker and farther from the flame.

254. Equations for Scheme for Group VI.—The following list contains the equations for all the reactions taking place in the analysis of the solution containing the three members of Group VI.

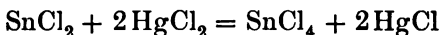
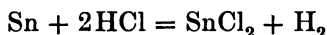
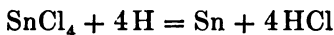
255. Precipitation with H_2S .



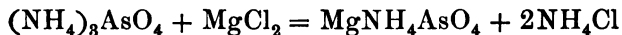
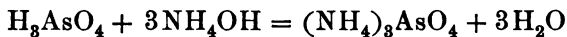
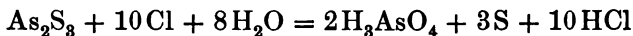
256. Dissolving the Sb and Sn residue in HCl.



257. Test for Sn.



258. Test for As.



GROUPS I, II, III, IV, V, AND VI TOGETHER

259. A solution containing Groups I, II, III, IV, V, and VI together is analyzed in much the same way that a solution containing Groups I, II, III, IV, and V was analyzed. First HCl is added, and this throws out Ag, Pb, and mercurous Hg; H_2S

is then passed in, and this throws out the sulphides of the other members of Group V, together with the sulphides of As, Sb, and Sn. The mixed sulphides are treated with yellow ammonium sulphide; this dissolves out the sulphides of Group VI, which may thus be filtered off from the members of Group V. The addition of HCl to the yellow ammonium sulphide solution reprecipitates the sulphides of Group VI, and this precipitate is treated exactly as was the precipitated sulphides in the scheme for Group VI. The residue left behind by the ammonium sulphide contains the other members of Group V, and is treated as was the corresponding precipitate in the scheme for Group V. The filtrate obtained from the precipitate caused by H_2S is then treated exactly as a solution containing Groups I to IV together. The procedure for a solution containing all six groups is contained in the following scheme for separating all the metals into groups. This is the last scheme we shall have for combinations of groups of bases. This scheme for separating all the bases into groups is, it will be seen easily, a key to all the work on basic analysis done this year; in addition, it brings to a close the work on bases alone. The modification treated in sections 272 to 287 will be omitted for the present and may be referred to later when the student meets insoluble phosphates and oxalates in his salt analysis. As soon as we have analyzed an unknown solution containing all six groups of bases we shall proceed immediately to the study of acid analysis, which will be found a very short subject compared with the basic analysis we are just completing. On looking at the scheme in section 260 you will see that the larger part of it relates to the separation of Groups V and VI from each other; this is the fussiest part of the whole scheme, and the student will need to exercise the greatest care and watchfulness at this point in the analysis. Remember the unstableness of the sulphides of ammonium and the ease with which acids precipitate sulphur from these liquids; you will then be less likely to confuse precipitated sulphur with the precipitated sulphides of the metals of Group VI.

Scheme for Separating all Bases into Groups

260.

To a solution containing the metals of all six groups add cold dilute HCl^o in excess. Filter, and save both precipitate and filtrate.

<p>P. Contains AgCl, PbCl₂, HgCl. Proceed as with corresponding precipitate in Scheme for Group V. See section 179.</p>	<p>F. Contains all the other metals. Transfer to a flask, and pass H₂S^o into the hot^c slightly acid solution with constant shaking until the odor of H₂S is distinctly perceptible after shaking and standing a few minutes. Filter, and save both precipitate and filtrate.^o</p> <p>P. Contains PbS, HgS, CdS, CuS, Bi₂S₃, As₂S₃, Sb₂S₃, SnS, and SnS₂. Wash with hot water till the wash-water is no longer acid.^o Divide the precipitate into two parts: (a) the smaller and (b) the larger. Treat (a) in a test tube with a few drops of dilute yellow^o (NH₄)₂S₂ and warm gently; if the precipitate dissolves, Group V is absent. If it does not dissolve, Group V is present and Group VI may be; filter, and to the clear filtrate add dilute HCl till it turns blue litmus paper red; a white precipitate is only S, and shows Group VI absent; in that case proceed with (b) as with the precipitated sulphides of Group V. If the precipitate is yellowish or orange,^o Group VI is probably present, and (b) must be treated with successive small portions of yellow (NH₄)₂S₂ till the filtrate from the last treatment gives a white precipitate with HCl. Combine the separate filtrates containing Group VI.</p>	<p>F. Contains Groups I, II, III, and IV. Warm in a flask and add NH₄Cl, NH₄OH till alkaline, then (NH₄)₂S. Filter, and save both precipitate and filtrate.</p>
	<p>P. Contains AlO₃H₃, CrO₃H₃, FeS, CoS, NiS, MnS, and ZnS. Proceed as with the corresponding precipitate in Scheme for Groups III and IV. See sections 100, 101, and 102.</p>	<p>F. Contains Groups I and II. Heat, and add (NH₄)₂CO₃ in excess. Filter, and save both precipitate and filtrate.</p>
	<p>F. Contains As, Sb, and Sn dissolved in yellow (NH₄)₂S₂. Add dilute HCl till solution is acid.</p> <p>P. Contains As₂S₃, Sb₂S₃, and SnS₂. Proceed as with the precipitated sulphides in Scheme for Group VI. See section 238.</p>	<p>P. Contains BaCO₃, SrCO₃, CaCO₃. Proceed as with the corresponding precipitate in Scheme for Groups I and II. See section 74.</p>
<p>Residue contains PbS, HgS, CuS, CdS, and Bi₂S₃. Wash well with water till the wash-water is no longer alkaline in order to get rid of (NH₄)₂S₂.^o Then proceed as with the corresponding precipitate in the Scheme for Group V. See section 179.</p>		<p>F. Contains Mg and Group I. Divide into (a) the smaller and (b) the larger portion, and proceed as in the Scheme for Groups I and II. See section 74.</p>

261. Notes on Scheme for Groups I, II, III, IV, V, and VI together. — The following notes will be found of service in the analysis of a solution containing the metals of all six groups; they refer mainly to the presence of Group VI with those groups already studied, and to the precautions necessary in separating Group VI from Group V. The notes on preceding groups all hold good here.

262. When cold dilute HCl is added to the original solution, a fine white precipitate may come down which is not AgCl , PbCl_2 , or HgCl , but an oxychloride of Bi or Sb; this BiOCl or SbOCl is produced on account of the dilution of the original solution by the water of the dilute HCl. These oxychlorides are soluble in an excess of HCl; it is not necessary to add more HCl to dissolve these precipitates, for H_2S readily changes them to Bi_2S_3 and Sb_2S_3 . See also section 221.

263. Before beginning to pass H_2S into the solution, it is well to test it with litmus paper. If the solution contains free HNO_3 or concentrated HCl, the H_2S will be decomposed with the separation of S, and sometimes with the evolution of NO_2 fumes. If the solution is strongly acid, it should be evaporated nearly to dryness and the residue dissolved in water, with the addition of a few drops of HCl if necessary; then pass in H_2S .

264. Have the solution hot, but not boiling, into which H_2S is passed, because a boiling acid solution is apt to dissolve the sulphides precipitated here.

265. The filtrate from the precipitated sulphides of Groups V and VI contains Groups I to IV, but it may also contain small amounts of Pb, Cd, Sb, and Sn, if the solution was too strongly acid before passing in the H_2S . It is advisable, therefore, to dilute a little of this filtrate with water and pass in some more H_2S ; if no precipitate forms, all is well; if a precipitate does form, the rest of the filtrate should be treated the same way, because any member of Group V or VI not entirely removed by H_2S is likely to appear in Group IV work and confuse the tests there.

266. Wash with hot water till the wash-water is no longer acid, first to prevent precipitation of much S when yellow $(\text{NH}_4)_2\text{S}_2$ is added, and second to get rid of any members of Groups III and

IV that may be occluded in the precipitate, because such members will be precipitated by the $(\text{NH}_4)_2\text{S}_2$ and appear in the Group V work.

267. Divide the precipitate into two parts if there is considerable of it. If there is only a little of it, a better way is to break the point of the filter, wash the precipitate into a test tube with water, add to the emulsion a very little yellow $(\text{NH}_4)_2\text{S}_2$, warm, filter, and make the preliminary test with HCl for Group VI in the filtrate.

268. Yellow $(\text{NH}_4)_2\text{S}_2$ must be used to dissolve Group VI, for the colorless $(\text{NH}_4)_2\text{S}_2$ does not dissolve SnS readily.

269. If the precipitate is yellowish or orange, and there is any doubt about it, add dilute HCl to some dilute yellow $(\text{NH}_4)_2\text{S}_2$, and compare the precipitated S formed here with the precipitate in question. CuS dissolves slightly in yellow $(\text{NH}_4)_2\text{S}_2$, and is reprecipitated therefrom by HCl as a dirty brownish precipitate.

270. Wash Group V sulphides till free from $(\text{NH}_4)_2\text{S}_2$ in order to prevent the precipitation of much S in subsequent treatment with nitric acid.

271. Precipitate contains Groups III and IV. If the original solution contains phosphates or oxalates of the members of Group II in solution by virtue of some free acid present, they will stay in solution until NH_4OH is added; then they will drop out along with the precipitate containing Groups III and IV on account of their insolubility in neutral or alkaline solutions. If there is reason to suspect the presence of such phosphates or oxalates, the Scheme for Groups III and IV must be modified a little and the solution analyzed according to the method given in section 277.

MODIFICATION OF SCHEME FOR GROUPS III AND IV IN THE PRESENCE OF PHOSPHATES AND OXALATES OF THE ALKALINE-EARTH METALS

272. In the regular work for Groups III and IV the addition of NH_4OH precipitates the hydrates of Al, Cr, and Fe, while $(\text{NH}_4)_2\text{S}$ completes the precipitation, throwing down the hydrates of Al and Cr and the sulphides of the other members. Mg and the alkaline-earth metals are not ordinarily precipitated by NH_4OH and $(\text{NH}_4)_2\text{S}$, because their hydrates and sulphides are soluble in water.

273. The above is true only when phosphates and oxalates are absent. Let us consider calcium phosphate a moment. This salt is insoluble in water but soluble in acids; *e.g.* $\text{CaHPO}_4 + 2\text{HCl} = \text{CaCl}_2 + \text{H}_3\text{PO}_4$. The solution obtained by dissolving calcium phosphate in hydrochloric acid contains calcium chloride and the excess of hydrochloric acid; the phosphoric acid formed is also in solution. If NH_4OH be added to this solution, it first neutralizes the excess of hydrochloric acid and then perhaps unites with some of the phosphoric acid, forming ammonium phosphate. At any rate the conditions are just the same as if ammonium phosphate were added to a neutral solution of calcium chloride, *i.e.* a precipitate of calcium phosphate forms. The phosphates and oxalates of Ba, Sr, Ca, and Mg all act this same way.

274. Suppose now that the filtrate from Groups V and VI contains some calcium phosphate held in solution by an excess of hydrochloric acid. It is evident, therefore, that NH_4OH will precipitate, not only the hydrates of Al, Cr, and Fe if they are present, but also the calcium phosphate. If, then, NH_4OH produces a precipitate, special tests for H_3PO_4 and $\text{H}_2\text{C}_2\text{O}_4$ must first be made as follows: To some of the filtrate from Groups V and VI, free from H_2S , add a few drops of HNO_3 and boil to oxidize the iron; divide into two parts; to one part add an equal volume of $(\text{NH}_4)_2\text{MoO}_4$ solution; a yellow precipitate forming at once, or on gentle warming if the solution is dilute, shows the presence of H_3PO_4 ; to the other part add some concentrated $\text{NaC}_2\text{H}_3\text{O}_2$ solution, a little $\text{HC}_2\text{H}_3\text{O}$, and some $\text{CaSO}_4 + \text{Aq}$; a white precipitate of CaC_2O_4 shows the presence of $\text{H}_2\text{C}_2\text{O}_4$. These tests are given in full in the scheme below.

275. If H_3PO_4 and $\text{H}_2\text{C}_2\text{O}_4$ are absent, the regular scheme for Groups III and IV may be used. See sections 100, 101, and 102.

276. If H_3PO_4 and $\text{H}_2\text{C}_2\text{O}_4$ are present, the solution must be tested for Ba, Sr, and Ca, before being treated with BaCO_3 emulsion. The scheme below takes account of only H_3PO_4 , because $\text{H}_2\text{C}_2\text{O}_4$ is not so frequently met with, and it acts exactly like phosphoric acid. It will be noticed that the scheme

Divide the filtrate from Groups V and VI into two parts, — (a) about one fourth and

Boil (a) till all H_2S is expelled.^o Add a few drops of HNO_3 and boil again to oxidize the iron. Divide this solution into three parts, — (1), (2), and (3).

To (1) add a little NH_4Cl and enough NH_4OH to make it slightly alkaline. If no precipitate forms immediately, heat to boiling, and allow to stand a few minutes.	To (2) add an equal amount of $(\text{NH}_4)_2\text{MoO}_4$ solution, shake well, and let stand a few minutes. P. Yellow, $(\text{NH}_4)_2\text{PO}_4$. 12 MoO_3 . $\therefore \text{H}_3\text{PO}_4$ pres.	To (3) add some concentrated $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ + Aq to destroy any free HCl or HNO_3 ; then add a little $\text{HC}_2\text{H}_3\text{O}_2$ and some CaSO_4 + Aq. P. White, CaC_2O_4 . $\therefore \text{H}_2\text{C}_2\text{O}_4$ pres.
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P. AlO_3H_3 , CrO_3H_3 , FeO_3H_3 , and phosphates and oxalates of Ba, Sr, Ca, and Mg. If NH_4OH produced a precipitate, try the tests for H_3PO_4 and

$\text{H}_2\text{C}_2\text{O}_4$ in (2) and (3); and if either is found present, use the rest of this scheme; if both are absent, use the regular Scheme for Groups III and IV. See Sections 100, 101, and 102.

Put (b) in a 250 c.c. flask. Add about 20 c.c. NF . Then add $(\text{NH}_4)_2\text{S}$ to complete precipitation. Heat. Filter through a plaited filter, and wash with hot water.

P. Contains AlO_3H_3 , CrO_3H_3 , FeS , CoS , NiS , MnSrC_2O_4 , CaC_2O_4 . Pour dilute HCl on the precipitate into a beaker with as little water as possible. Let stand.

Residue is CoS and NiS . Analyze this according to the method given for the residue containing CoS and NiS in the Scheme for Groups III and IV. See sections 100, 101, and 102.

F. Contains AlCl_3 , CrCl_3 , FeCl_3 , MnCl_2 , HNO_3 and boil to oxidize the iron. Divide (c) the larger part.

Evaporate (a) to small bulk and add dilute H_2SO_4 . ^o Filter.		Dilute (b) with water and add $\text{K}_4\text{Fe}(\text{CN})_6$.		T tate of the can water All
P. BaSO_4 and SrSO_4 (and a little CaSO_4). Moisten a platinum test wire with HCl , dip it into the precipitate and try the flame test. ^o Yellow-green. $\therefore \text{Ba}$ pres. Red. $\therefore \text{Sr}$ pres.	F. Add three times its volume of alcohol. ^o	P. Dark blue. $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. $\therefore \text{Fe}$ pres. If Fe is present, test small portions of the original solution with $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_6\text{Fe}_2(\text{CN})_{12}$ to find out which kind of Fe is present.		P and dilu and to dilu P BaS reje
	P. White CaSO_4 . Confirm by dissolving the precipitate in water and adding $(\text{NH}_4)_2\text{C}_2\text{O}_4$. P. White CaC_2O_4 . $\therefore \text{Ca}$ pres.			

IV when H_3PO_4 and $H_2C_2O_4$ are present

h and (b) the rest.

c. NH_4Cl , and then enough NH_4OH to make it slightly alkaline or to cause a slight precipitate. Heat to boiling, and shake occasionally for 10 or 15 minutes, or till the precipitate is granular. Let water containing a few drops of $(NH_4)_2S$.

S, MnS , ZnS , $AlPO_4$, $CrPO_4$, $Ba_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ca_3(PO_4)_2$, $MgNH_4PO_4$, BaC_2O_4 , precipitate in the filter paper, break the paper at the point, and wash the mixture down. Let stand for some minutes. Filter.

$MnCl_2$, $ZnCl_2$, $BaCl_2$, $SrCl_2$, $CaCl_2$, $MgCl_2$, H_3PO_4 , and $H_2C_2O_4$. Add a few drops of Divide this solution into three parts, (a) about one fourth, (b) a few drops only, and

To (c) add $FeCl_3 + Aq^\circ$ carefully till a drop of the solution gives a yellowish precipitate when put into a little NH_4OH on a watch glass. Evaporate the solution till most of the free acid is expelled. Add $Na_2CO_3 + Aq$ as long as the precipitate which forms can be made to redissolve on shaking. Put the solution in a 250 c.c. flask, dilute with water to 200 c.c., cool if still hot, and add $BaCO_3$ emulsion, avoiding large excess. Allow to stand with frequent shaking for half an hour. Filter.

P. FeO_3H_3 , AlO_3H_3 , CrO_3H_3 , $FePO_4$, and excess of $BaCO_3$. Dissolve in dilute HCl on the filter, break the paper, and wash through into the beaker; heat to boiling and without filtering add dilute H_2SO_4 in excess. Filter.

P White
 $BaSO_4$;
reject
F. Contains $FeCl_3$, $AlCl_3$, $CrCl_3$, and H_3PO_4 . Add $NaOH$ in excess, and boil a few minutes. Filter.

P. FeO_3H_3 and CrO_3H_3 . Dissolve the precipitate in dilute HCl . Add a very little Na_2O_2 and boil till effervescence ceases. The liquid contains Cr as Na_2CrO_4 . Acidify it with HCl and add $Pb(C_2H_3O_2)_2$.

P. Yellow, $PbCrO_4$.
 $\therefore Cr$ pres.

F. Contains Na_2AlO_3 and sodium phosphate. Make acid with HCl . Add NH_4OH till alkaline.

P. White, $AlPO_4$.
 $\therefore Al$ pres.

F. Contains $MnCl_2$, $ZnCl_2$, $BaCl_2$, $SrCl_2$, $CaCl_2$, and $MgCl_2$. Add NH_4OH till slightly alkaline, then $(NH_4)_2S$ to complete precipitation, but not in large excess. Filter.

P. MnS and ZnS .
Wash into a beaker with HCl and boil till H_2S is all expelled. Add $NaOH$ in excess and filter.

P. MnO_2H_2 . Fuse on Pt foil with six times as much dry Na_2CO_3 . Mass turns green from Na_2MnO_4 formed.
 $\therefore Mn$ pres.

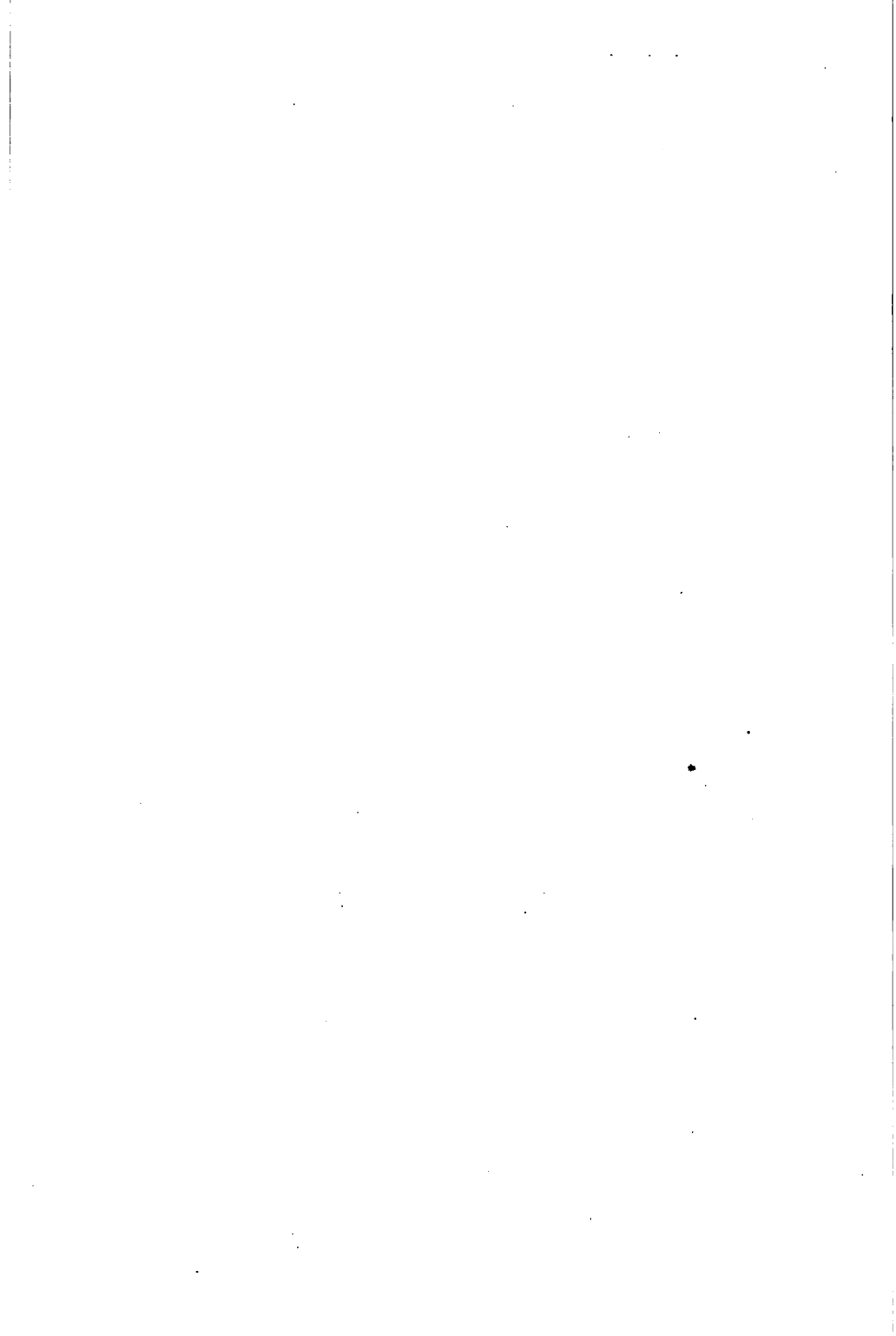
F. Contains Na_2ZnO_2 . Pass in a little H_2S .
P. White, ZnS .
 $\therefore Zn$ pres.

F. Contains $BaCl_2$, $SrCl_2$, $CaCl_2$, and $MgCl_2$. Heat a little and add $(NH_4)_2CO_3$ and $(NH_4)_2C_2O_4$. Filter.

P. $BaCO_3$, $SrCO_3$, $CaCO_3$, CaC_2O_4 . Reject.
F. Contains $MgCl_2$. Evaporate to small bulk. Add half its volume of NH_4OH . Then add Na_2HPO_4 .

P. White, $MgNH_4PO_4$.
 $\therefore Mg$ pres.

F. Contains Groups I and II. Proceed as in the Scheme for Groups I and II. See section 74.



given here for the analysis of a Groups III and IV solution in the presence of phosphoric and oxalic acids consists largely of the regular scheme used when Cr is present, with the addition of only a very little material.

278. Notes on Scheme for Groups III and IV when H_3PO_4 and $\text{H}_2\text{C}_2\text{O}_4$ are Present. — The following notes will be found of service as they present certain details that could not be given in the scheme.

279. Boil (a) till all H_2S is expelled, otherwise $(\text{NH}_4)_2\text{S}$ will be formed when NH_4OH is added and the test will be of no value.

280. Add dilute H_2SO_4 in order to show the presence of the alkaline-earth metals; this is necessary because BaCO_3 is put in later as a reagent. The H_2SO_4 throws down all the Ba and Sr; also part of the Ca if the solution is concentrated.

281. The flame test for Ba and Sr is satisfactory if either is present alone; it may be satisfactory even if both are present. Occasionally it is advisable to fuse the precipitate containing BaSO_4 and SrSO_4 with Na_2CO_3 , boil with water, filter, treat the residual BaCO_3 and SrCO_3 with HNO_3 , and in the resulting liquid try the regular Group II tests for Ba and Sr.

282. Add three times its volume of alcohol to the solution containing Ca, because CaSO_4 is slightly soluble in water but insoluble in alcohol.

283. Add $\text{FeCl}_3 + \text{Aq}$ in order to prevent the phosphates of the alkaline-earth metals from precipitating when BaCO_3 is added. The FeCl_3 reacts easily with the H_3PO_4 , giving insoluble FePO_4 , and allows the Group II metals to go into the filtrate. The test with NH_4OH shows when enough FeCl_3 has been added to react with all the H_3PO_4 ; before that point is reached, white FePO_4 precipitates; but as soon as an excess of FeCl_3 is present, brown FeO_3H_3 drops out.

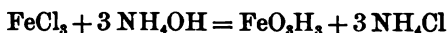
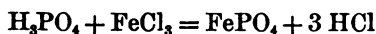
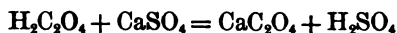
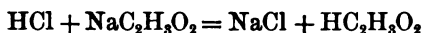
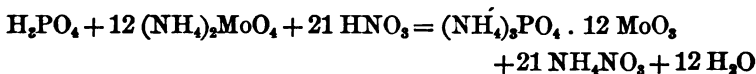
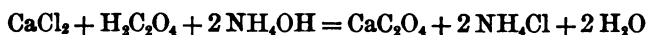
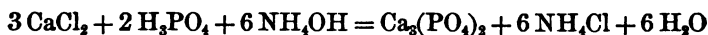
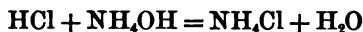
284. The MnS and ZnS precipitate should be light colored. If it is dark, it shows that some FeS has run through to this point because the Fe was not completely oxidized with HNO_3 .

285. Add $(\text{NH}_4)_2\text{CO}_3$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in order to remove Ba, Sr, and Ca before testing for Mg, otherwise their phosphates, which are insoluble, would appear when Na_2HPO_4 is added later in the

test for Mg. $(\text{NH}_4)_2\text{CO}_3$ precipitates all the Ba and Sr and most of the Ca. The $(\text{NH}_4)_2\text{C}_2\text{O}_4$ is added to remove any Ca that may have escaped precipitation as the carbonate, for calcium oxalate is more insoluble than calcium carbonate.

286. Contains Groups I and II. Although tests have already been made for Ba, Sr, Ca, and Mg, these metals may also appear in their proper places in Group II. Therefore the Group II work must not be omitted. If calcium phosphate is the only salt of an alkaline-earth metal present, then all the Ca will drop out as calcium phosphate when NH_4OH is added to the filtrate from Group V, because there is just the proper amount of the phosphoric acid radical present to unite with all the Ca present. Suppose, however, the original solution contained calcium chloride or calcium nitrate in addition to calcium phosphate held in solution by HCl. In that case, when NH_4OH is added, all the phosphoric acid radical will come down as calcium phosphate, using as much of the Ca as it needs to form the phosphate. The excess of Ca that it does not need will stay in solution, and this, which amounts theoretically to the amount of Ca in the calcium chloride or calcium nitrate, will appear in the filtrate which is tested for Group II.

287. The equations for this scheme are practically a repetition of those given under the scheme for Groups III and IV when Cr is present. Because of the presence of phosphoric and oxalic acids a few more reactions take place, and these are represented by the following equations:



PART III

ACID ANALYSIS

LIST OF ACIDS BY GROUPS

288. Only the more common acids, or acid radicals, will be tested for in the study of unknown substances. In general, inorganic acids only should be studied, and organic acids should be omitted entirely; but the three organic acids, oxalic, tartaric, and acetic, are so common and so many of their salts are known, that it seems advisable to include these three acids. The following list shows the division of acids into three groups, the first two groups being characterized by the action of the group reagent with the solution containing the acid radical; there is no group reagent for the last group.

	FORMULA	NAME	NAME OF SALTS
289. Group I.	H_2CrO_4	Chromic acid	Chromates
The	H_3AsO_3	Arsenous acid	Arsenites
BaCl_2	H_3AsO_4	Arsenic acid	Arsenates
Group.	H_2SO_3	Sulphurous acid	Sulphites
	$\text{H}_2\text{S}_2\text{O}_3$	Thiosulphuric acid	Thiosulphates
	H_3PO_4	Phosphoric acid	Phosphates
	H_3BO_3	Boric acid	Borates
	$\text{H}_2\text{C}_2\text{O}_4$	Oxalic acid	Oxalates
	HF	Hydrofluoric acid	Fluorides
	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	Tartaric acid	Tartrates
	H_2CO_3	Carbonic acid	Carbonates
	H_4SiO_4	Silicic acid	Silicates
	H_2SO_4	Sulphuric acid	Sulphates
290. Group II.	HCl	Hydrochloric acid	Chlorides
The	HBr	Hydrobromic acid	Bromides
AgNO_3	HI	Hydriodic acid	Iodides
Group.	HCN	Hydrocyanic acid	Cyanides
	$\text{H}_4\text{Fe}(\text{CN})_6$	Hydroferrocyanic acid	Ferrocyanides
	$\text{H}_6\text{Fe}_2(\text{CN})_{12}$	Hydroferricyanic acid	Ferricyanides
	H_2S	Hydrosulphuric acid	Sulphides

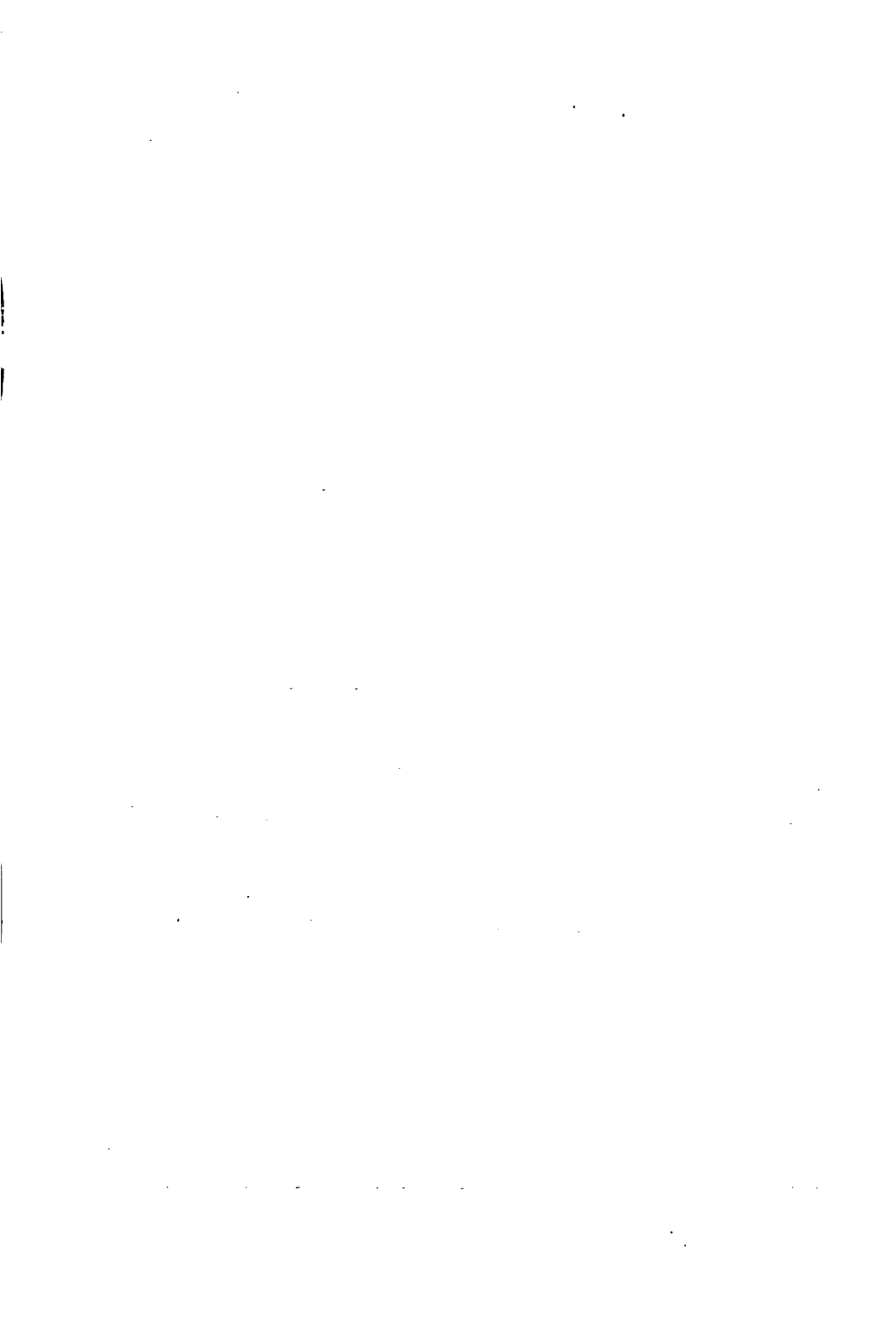
	FORMULA	NAME	NAME OF SALTS
291. Group III.	HNO_3	Nitric acid	Nitrates
	HClO_3	Chloric acid	Chlorates
	$\text{HC}_2\text{H}_3\text{O}_2$	Acetic acid	Acetates

292. Preliminary Work.—Take in twenty-three test tubes small portions, about 10 c.c. each, of solutions containing the twenty-three acid radicals to be studied. It is customary not to use the acids themselves, as many of them do not form satisfactory solutions to keep for general use. Soluble salts of these acids all give the proper reactions; it is customary, therefore, to use the sodium salts throughout, though occasionally potassium or ammonium salts may be substituted to advantage. To each of the solutions in the twenty-three test tubes add a little $\text{BaCl}_2 + \text{Aq}$. Note in which test tubes precipitates occur; also note the color and form of each precipitate. Divide the barium chromate precipitate into three parts by shaking up the emulsion and pouring it into three different test tubes; in these tubes try the solubility of the precipitate in the three acids, hydrochloric, nitric, and acetic. In like manner try the solubility in these three acids of all the precipitates caused by barium chloride.

293. In twenty-three clean test tubes again put small portions of the solutions containing the acid radicals, and repeat with $\text{CaCl}_2 + \text{Aq}$ all the experiments tried with $\text{BaCl}_2 + \text{Aq}$.

294. Again take in twenty-three test tubes small portions of the acid radical solutions and add to each $\text{AgNO}_3 + \text{Aq}$. Note as before the color and form of each precipitate; try the solubility of each precipitate in nitric acid and in aqua ammonia; in addition try the solubility of the silver salts of Group II acids in an aqueous solution of potassium cyanide.

295. At the top of each column in the following table comes first the formula of the acid under consideration and then the formula of the salt of that acid used. The best strength of solution to use is generally 1:40, but in a few cases other concentrations are necessary. Verify all the results given in the following table.

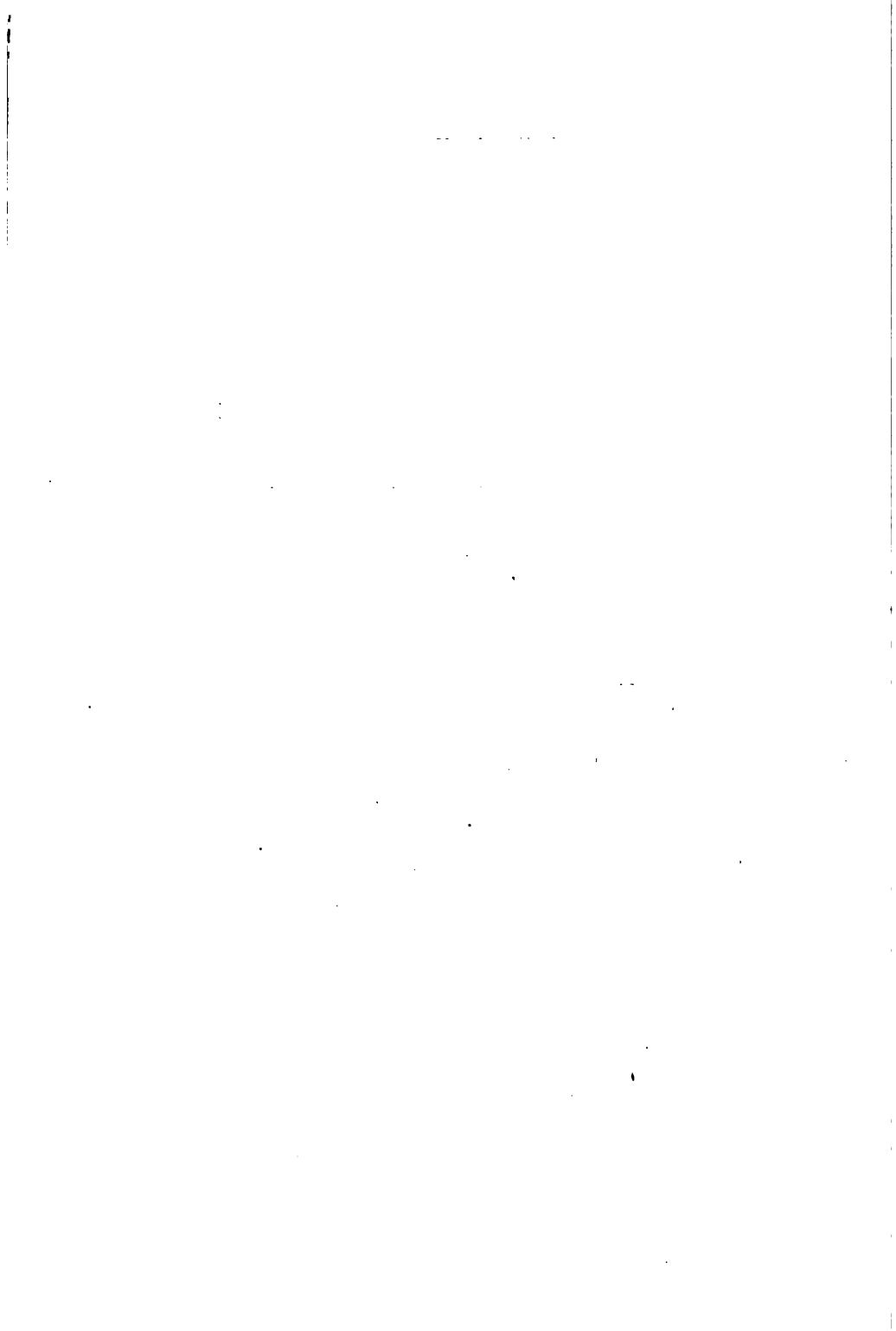


Reagent	H_2CrO_4 K_2CrO_4	H_3AsO_3 Na_3AsO_3	H_3AsO_4 Na_3AsO_4	H_2SO_3 Na_2SO_3	$H_2S_2O_3$ $Na_2S_2O_3$	H_3PO_4 Na_2HPO_4	H_3B (H_2B_4 Na_2B_{10})
$BaCl_2 + Aq.$	Yellow ppt., $BaCrO_4$; sol. in HCl and in HNO_3 ; insol. in $HC_2H_3O_2$.	White ppt., $Ba_3(AsO_3)_2$; sol. in HCl, HNO_3 , and $HC_2H_3O_2$.	Slow white ppt., $Ba_3(AsO_4)_2$; sol. in HCl, HNO_3 , and $HC_2H_3O_2$.	White ppt., $BaSO_3$; sol. in HCl and in HNO_3 ; partly sol. in $HC_2H_3O_2$.	White ppt., BaS_2O_3 ; only from conc. solution; acids ppt. S.	White ppt., $BaHPO_4$; sol. in HCl, HNO_3 , and $HC_2H_3O_2$.	White ppt., $Ba(BO_2)_2$; difficult to dissolve in water; in HCl, HNO_3 , and $HC_2H_3O_2$.
$CaCl_2 + Aq.$	No ppt.	White ppt., $Ca_3(AsO_3)_2$; sol. in HCl, HNO_3 , and $HC_2H_3O_2$.	White ppt., $Ca_3(AsO_4)_2$; sol. in HCl, HNO_3 , and $HC_2H_3O_2$.	White ppt., $CaSO_3$; sol. in HCl, HNO_3 , and $HC_2H_3O_2$.	No ppt.	White ppt., $CaHPO_4$; sol. in HCl, HNO_3 , and $HC_2H_3O_2$.	White ppt., $Ca(BO_2)_2$; sol. in HNO_3 , and $HC_2H_3O_2$.
$AgNO_3 + Aq.$	Dark red ppt., Ag_2CrO_4 ; sol. in HNO_3 and NH_4OH .	Yellow ppt., Ag_3AsO_3 ; sol. in HNO_3 and NH_4OH .	Reddish brown ppt., Ag_3AsO_4 ; sol. in HNO_3 and NH_4OH .	White ppt., Ag_2SO_3 ; sol. in Na_2SO_3 + Aq; decomp. by boiling into Ag, Ag_2SO_4 , and SO_2 ; sol. in HNO_3 and NH_4OH .	White ppt., $Ag_2S_2O_3$; sol. in $Na_2S_2O_3$ + Aq; decomp. by water into H_2SO_4 and Ag_2S .	Yellow ppt., Ag_3PO_4 ; sol. in HNO_3 and NH_4OH .	White ppt., $AgBO_2$; in HNO_3 and NH_4OH .

Reagent	HCl NaCl	HBr KBr	HI NaI	HCN KCN	$H_2Fe(CN)_6$ K ₄
$BaCl_2 + Aq.$	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.
$CaCl_2 + Aq.$	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.
$AgNO_3 + Aq.$	White ppt., $AgCl$; insol. in HNO_3 ; sol. in NH_4OH and KCN + Aq.	Yellowish white ppt., $AgBr$; insol. in HNO_3 ; difficultly sol. in NH_4OH ; sol. in KCN + Aq.	Yellow ppt., AgI ; insol. in HNO_3 ; very difficultly sol. in NH_4OH ; sol. in KCN + Aq.	White ppt., $AgCN$; insol. in HNO_3 ; sol. in NH_4OH and KCN + Aq.	White ppt., $Ag_4Fe(CN)_6$; insol. in HNO_3 ; sol. in NH_4OH and KCN.

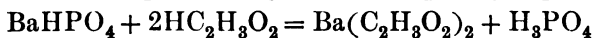
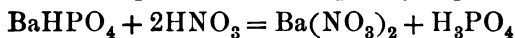
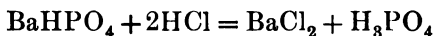
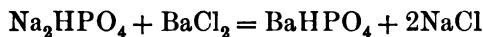
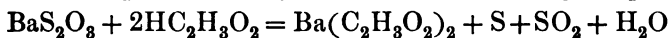
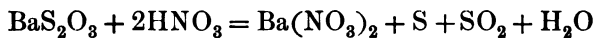
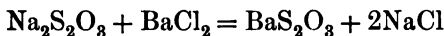
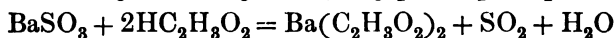
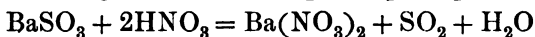
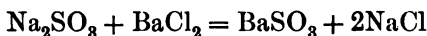
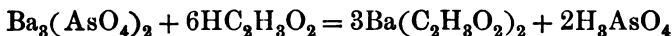
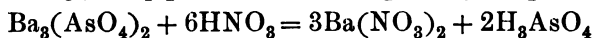
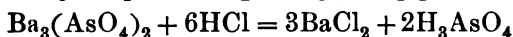
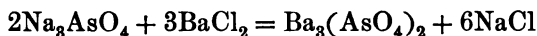
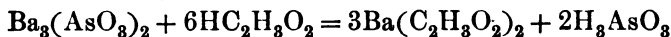
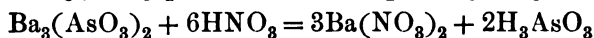
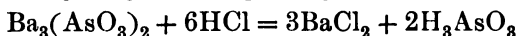
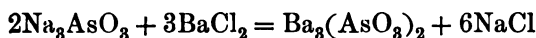
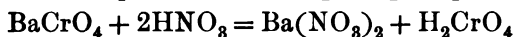
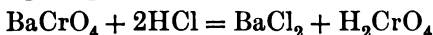
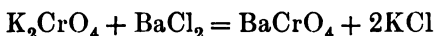
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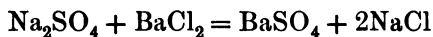
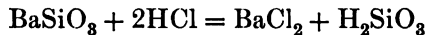
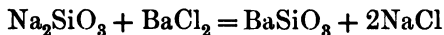
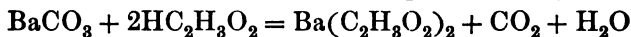
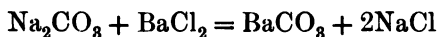
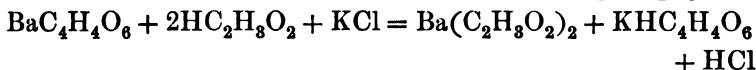
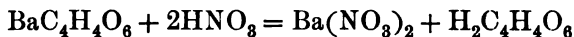
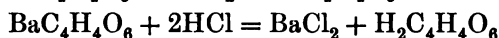
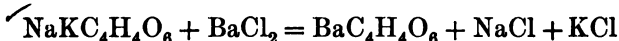
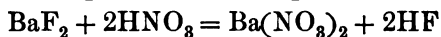
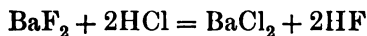
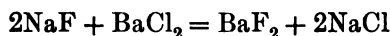
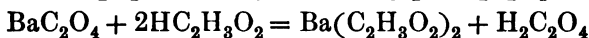
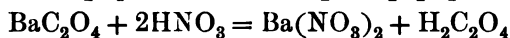
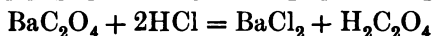
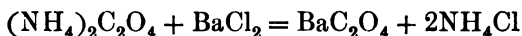
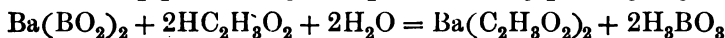
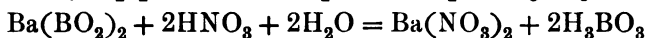
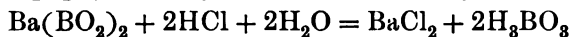
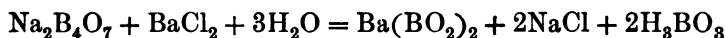
	$\text{H}_2\text{C}_2\text{O}_4$ $(\text{NH}_4)_2\text{C}_2\text{O}_4$	HF NaF	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ $\text{NaKC}_4\text{H}_4\text{O}_6$	H_2CO_3 Na_2CO_3	H_4SiO_4 (H_2SiO_3) Na_2SiO_3	H_2SO_4 Na_2SO_4
pt., 2; 7 sol. nd 2.	White ppt., BaC₂O₄ ; sol. in HCl, HNO ₃ , and HC ₂ H ₃ O ₂ .	White ppt., BaF₂ ; sol. in HCl and HNO ₃ ; insol. in HC ₂ H ₃ O ₂ .	White ppt., BaC₄H₄O₆ ; sol. in excess of BaCl ₂ or NaKC ₄ H ₄ O ₆ ; sol. in HCl and HNO ₃ ; HC ₂ H ₃ O ₂ ppts. KHC ₄ H ₄ O ₆ .	White ppt., BaCO₃ ; sol. in HCl, HNO ₃ , and HC ₂ H ₃ O ₂ .	White ppt., BaSiO₃ ; nearly sol. in HCl, HNO ₃ , and HC ₂ H ₃ O ₂ .	White ppt., BaSO₄ ; insol. in HCl, HNO ₃ , and HC ₂ H ₃ O ₂ .
pt., 2; Cl, nd 2.	White ppt., CaC₂O₄ ; sol. in HCl, and HNO ₃ ; insol. in HC ₂ H ₃ O ₂ .	White, gelatin- ous ppt., CaF₂ ; sol. in HCl, and HNO ₃ ; insol. in HC ₂ H ₃ O ₂ .	Slow white ppt., CaC₄H₄O₆ ; sol. in HCl, HNO ₃ , and HC ₂ H ₃ O ₂ .	White ppt., CaCO₃ ; sol. in HCl, HNO ₃ , and HC ₂ H ₃ O ₂ .	White ppt., CaSiO₃ ; sol. in HCl, HNO ₃ , and HC ₂ H ₃ O ₂ .	White ppt., CaSO₄ , in conc. solution; sl. sol. in water, HCl, and HNO ₃ ; insol. in HC ₂ H ₃ O ₂ .
pt., sol.	White ppt., Ag₂C₂O₄ ; sol. in HNO ₃ and NH ₄ OH.	No ppt.	White ppt., Ag₂C₄H₄O₆ ; sol. in HNO ₃ and NH ₄ OH; ppts. a mirror of Ag when warmed.	Gray ppt., Ag₂CO₃ ; sol. in HNO ₃ and NH ₄ OH.	Yellow ppt. in conc. solutions, Ag₂SiO₃ ; sol. in HNO ₃ and NH ₄ OH.	White ppt., only from conc. solution, Ag₂SO₄ .
Fe(CN)₆ Fe(CN)₆	H₆Fe₂(CN)₁₂ K₆Fe₂(CN)₁₂	H₂S (NH₄)₂S	HNO₃ KNO₃	HClO₃ KClO₃	HC₂H₃O₂ NaC₂H₃O₂	
	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	
	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	
pt., N ₆ ; insol. in ol. in NH ₄ OH + Aq.	Orange ppt., Ag₆Fe₂(CN)₁₂ ; insol. in HNO ₃ ; sol. in NH ₄ OH and KCN + Aq.	Black ppt., Ag₂S ; sol. in hot HNO ₃ .	No ppt.	No ppt.	White ppt., AgC₂H₃O₂ ; sol. in hot water.	



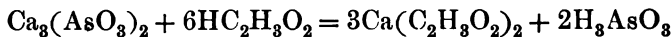
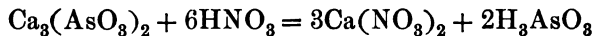
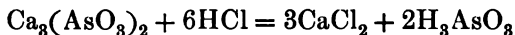
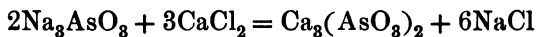
297. Equations for Preliminary Work for Acids.—The following list contains the equations for all the reactions taking place in the preliminary work for acids indicated in the preceding table.

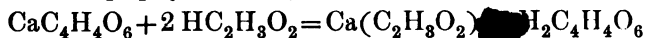
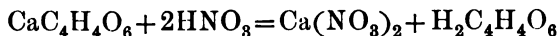
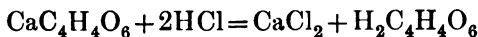
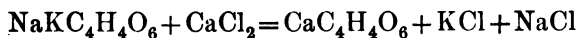
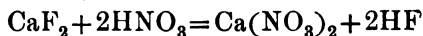
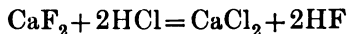
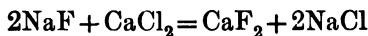
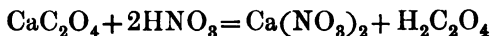
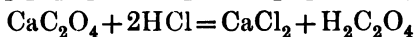
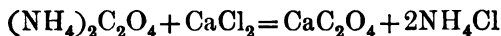
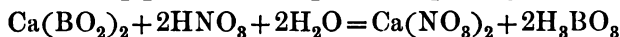
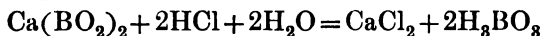
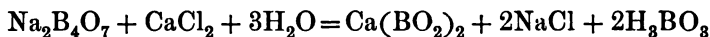
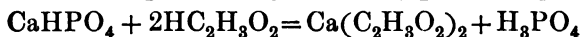
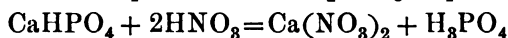
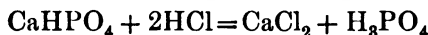
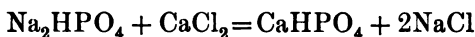
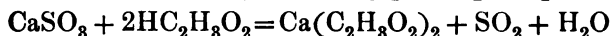
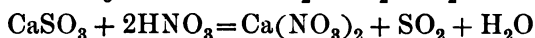
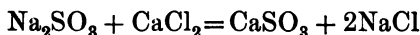
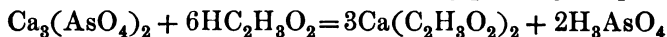
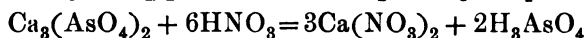
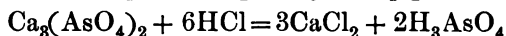
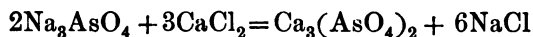
298. Precipitates produced by BaCl₂, and their solubilities in acids.

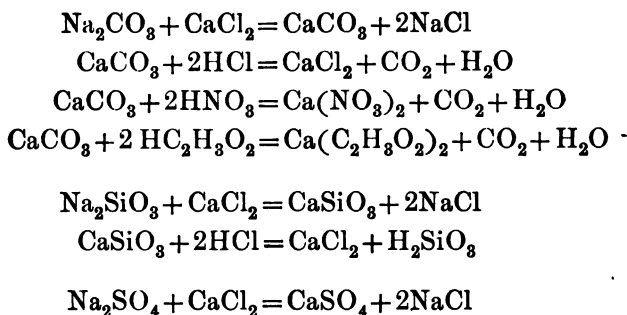




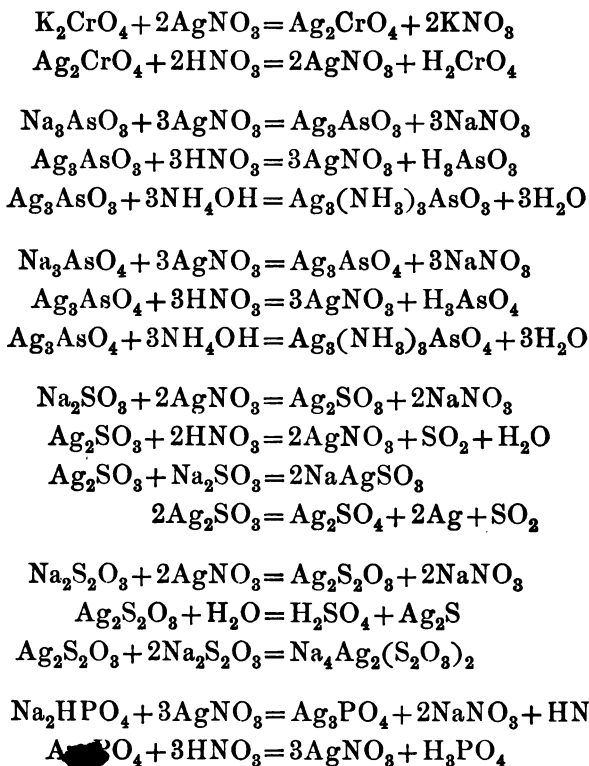
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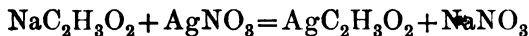
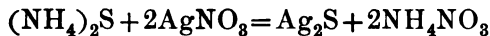
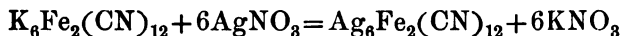
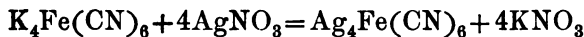
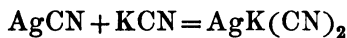
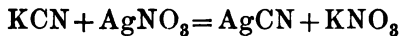
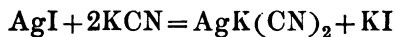
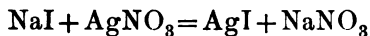
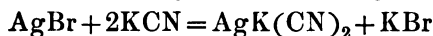
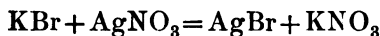
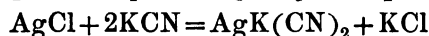
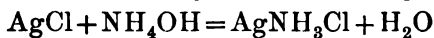
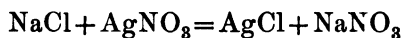
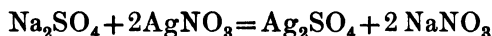
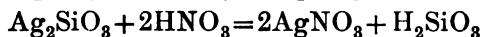
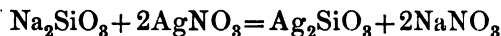
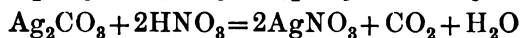
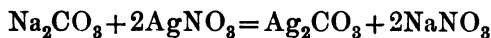
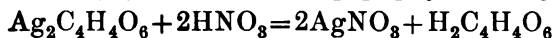
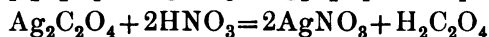
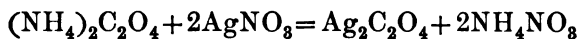
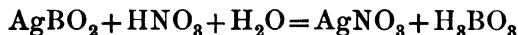
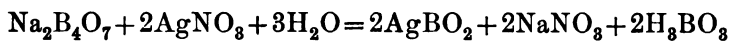






300. Precipitates produced by AgNO_3 , and their solubilities in HNO_3 and in other reagents.





301. Special Tests for Acids. — In basic analysis the general reagents separated the groups of bases from each other, and then each group-precipitate was separated into the different bases according to the proper schemes. Acids do not lend themselves readily to such separation. It is more convenient to show the presence or absence of the Groups I and II of acids by means of BaCl_2 and AgNO_3 , and then to try in separate portions of solution special tests for such acids as are not proved absent by the group reagent. This method is particularly convenient because the nature of the base present often excludes the presence of many acids; for instance, a metallic salt soluble in water cannot contain an acid radical that forms an insoluble salt with that metal; therefore, in a solution containing calcium, one need not test for a carbonate, an oxalate, or any other insoluble salt of calcium.

302. The following list contains the special tests for all the acids ordinarily studied in Qualitative Analysis. An examination of the list will show that many of the tests have already been tried in other places; such tests need not be repeated now. Tests that are new should be tried and verified.

303. H_2CrO_4 . *Chromic acid.* $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ throws down a yellow precipitate of PbCrO_4 , insoluble in $\text{HC}_2\text{H}_3\text{O}_2$.

304. H_3AsO_3 . *Arsenous acid.* From neutral solutions AgNO_3 precipitates pale yellow Ag_3AsO_3 . H_2S precipitates yellow As_2S_3 immediately from acid solutions.

305. H_3AsO_4 . *Arsenic acid.* From neutral solutions AgNO_3 precipitates red-brown Ag_3AsO_4 . H_2S precipitates yellow As_2S_3 very slowly from acid solutions.

306. H_2SO_3 . *Sulphurous acid.* HCl or H_2SO_4 evolves SO_2 from the dry salt or from its aqueous solution.

307. $\text{H}_2\text{S}_2\text{O}_3$. *Thiosulphuric acid.* HCl or H_2SO_4 evolves SO_2 from the dry salt or from its aqueous solution, and precipitates sulphur, first white and then yellow, from concentrated solutions.

308. H_3PO_4 . *Phosphoric acid.* In solutions of phosphates that are soluble in water, NH_4OH , NH_4Cl , and MgSO_4 pre-

precipitate white MgNH_4PO_4 , which is crystalline, and which separates slowly from dilute solutions. H_3AsO_4 gives a similar precipitate; therefore if As is present, it must first be removed by means of H_2S . To detect H_3PO_4 in salts soluble in acids only, dissolve the phosphate in HNO_3 and add a little of the solution to some $(\text{NH}_4)_2\text{MoO}_4$ (ammonium molybdate) solution. The yellow precipitate is ammonium phosphomolybdate; sometimes it comes down slowly.

309. H_3BO_3 . Boric acid. Into a solution of the borate, slightly acidified with HCl , dip a strip of turmeric paper. Dry the paper carefully at 100°C . The paper, when dried, is red, but changes to greenish black when moistened with $\text{Na}_2\text{CO}_3 + \text{Aq}$.

310. $\text{H}_2\text{C}_2\text{O}_4$. Oxalic acid. To a neutral or alkaline solution add $\text{HC}_2\text{H}_3\text{O}_2$ in excess; then add $\text{CaSO}_4 + \text{Aq}$, and let it stand awhile. A white precipitate of CaC_2O_4 shows the presence of oxalic acid. If the solution of the oxalate is acid with HCl or HNO_3 , add considerable $\text{NaC}_2\text{H}_3\text{O}_2 + \text{Aq}$; this destroys the acid and forms $\text{HC}_2\text{H}_3\text{O}_2$; then add $\text{CaSO}_4 + \text{Aq}$ as before.

311. HF. Hydrofluoric acid. Mix the fluoride in a perfectly dry test tube with an equal amount of SiO_2 (sand); add enough concentrated H_2SO_4 to form a paste and heat gently. When fumes arise, hold in them a glass rod wet with water. A white, gelatinous coating of H_4SiO_4 on the rod indicates a fluoride.

312. $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. Tartaric acid. Make a very strong solution of the tartrate, acidify slightly with $\text{HC}_2\text{H}_3\text{O}_2$, add some $\text{KC}_2\text{H}_3\text{O}_2$ solution and allow to stand awhile. A white crystalline precipitate of $\text{KHC}_4\text{H}_4\text{O}_6$ indicates a tartrate.

313. H_2CO_3 . Carbonic acid. Add dilute HCl to the dry salt or to a strong aqueous solution of the salt in a test tube. If a gas is evolved, hold a glass rod with a drop of $\text{BaO}_2\text{H}_2 + \text{Aq}$ at the end of it, just above the surface of the liquid in the test tube. A milkyiness on the wet rod is due to the formation of BaCO_3 and indicates a carbonate.

314. H_4SiO_4 and H_2SiO_3 . *Silicic acid*. When concentrated HCl is added to a solution containing a silicate, gelatinous H_4SiO_4 usually separates; it is verified by evaporating to dryness, when gritty SiO_2 is left. Insoluble silicates should be fused with Na_2CO_3 ; this yields Na_2SiO_3 and the oxide or the carbonate of the metal which was in the original silicate; if the resulting mixture is treated with water, the Na_2SiO_3 dissolves, and to this solution the test for silicic acid given above may be applied.

315. H_2SO_4 . *Sulphuric acid*. From a solution of a sulphate BaCl_2 throws out a white precipitate of BaSO_4 , which is insoluble in dilute HCl .

316. HCl . *Hydrochloric acid*. The dry salt, when mixed with MnO_2 and concentrated H_2SO_4 and heated, evolves Cl_2 ; this may be recognized by its color, odor, and bleaching action on test paper.

Test for HCl in the Presence of HBr and HI . — Powder the substance and mix well with dry powdered $\text{K}_2\text{Cr}_2\text{O}_7$; place the mixture in a test tube fitted with a cork and small delivery tube; cover the mixture with concentrated H_2SO_4 and heat. Dark red vapors of chromium oxychloride are formed; pass them into a test tube containing a little dilute NH_4OH ; the liquid becomes yellow, due to formation of $(\text{NH}_4)_2\text{CrO}_4$. If the color is not marked, acidify the solution with $\text{HC}_2\text{H}_3\text{O}_2$, and add $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. A yellow precipitate indicates the presence of $(\text{NH}_4)_2\text{CrO}_4$.

317. HBr . *Hydrobromic acid*. To a solution of a bromide in a test tube add a little CS_2 , then $\text{Cl}_2 + \text{Aq}$ drop by drop, shaking the tube; the liberated Br_2 dissolves in the CS_2 , coloring it red.

Test for HBr in the Presence of HI . — If HI is present with HBr , the above test for HBr gives violet-colored CS_2 , because $\text{Cl}_2 + \text{Aq}$ sets free all the iodine before any of the bromine. Then add $\text{Cl}_2 + \text{Aq}$, cautiously shaking the tube, and the violet I_2 color will gradually disappear, because the excess of chlorine oxidizes the iodine to colorless iodic acid. Then the bromine is set free, color-

ing the CS_2 red; more $\text{Cl}_2 + \text{Aq}$ will bleach the Br_2 color also; hence the need of adding the reagent very slowly.

318. HI. Hydriodic acid. Put in a test tube a little CS_2 , a little dilute HCl , a drop or two of $\text{KNO}_2 + \text{Aq}$, and shake. Then add a few drops of a solution of an iodide and shake. HCl liberates HNO_2 ; this in turn liberates I_2 from the iodide, and the I_2 colors the CS_2 violet.

319. HCN. Hydrocyanic acid. To a *very dilute* solution of a cyanide add concentrated H_2SO_4 . The almond-odored gas evolved is HCN , which is poisonous if not considerably diluted with air. Therefore smell cautiously.

320. A Safer Test.—To a solution of a cyanide add enough NaOH to make it alkaline if it is not already alkaline. Then add some $\text{FeSO}_4 + \text{Aq}$ and a few drops of $\text{FeCl}_3 + \text{Aq}$. Heat a little and then acidify with dilute HCl in order to dissolve the greenish black precipitate of ferroso-ferric hydrate. A blue precipitate remaining in the acid solution shows a cyanide was present in the original solution.

321. $\text{H}_4\text{Fe}(\text{CN})_6$. Hydroferrocyanic acid. Soluble ferrocyanides are recognized by adding $\text{FeCl}_3 + \text{Aq}$ to their solutions; dark blue $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ is formed. Insoluble ferrocyanides are rendered soluble by boiling with $\text{NaOH} + \text{Aq}$; the resulting solution may be tested with $\text{FeCl}_3 + \text{Aq}$ as above.

322. $\text{H}_6\text{Fe}_2(\text{CN})_{12}$. Hydroferricyanic acid. Soluble ferricyanides are recognized by adding freshly reduced $\text{FeSO}_4 + \text{Aq}$; dark blue $\text{Fe}_3\text{Fe}_2(\text{CN})_{12}$ is formed. Insoluble ferricyanides are rendered soluble by boiling with $\text{NaOH} + \text{Aq}$; the resulting solution may be tested with $\text{FeSO}_4 + \text{Aq}$ as above.

323. H_2S . Hydrosulphuric acid. HCl evolves H_2S from most sulphides; from those not decomposed by HCl alone, H_2S may be evolved by adding a little Zn with the HCl . The H_2S may be recognized by the odor or by the blackening of paper moistened with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.

324. HNO_3 . Nitric acid. Mix the solution to be tested with some cold concentrated freshly reduced $\text{FeSO}_4 + \text{Aq}$; then,

tipping the test tube, let some concentrated H_2SO_4 run down the side and form a layer at the bottom. A brown ring between the two layers shows the presence of a nitrate. A bromide or an iodide may produce a ring, but this will be either red or violet and distinctly different from the brown ring due to the presence of a nitrate.

325. HClO_3 . Chloric acid. Put the salt in a test tube, add enough water just to cover it, and then add a few drops of concentrated H_2SO_4 . The H_2SO_4 decomposes chlorates, with the formation of a yellowish green gas, ClO_2 , that resembles chlorine in odor and colors the solution strongly yellow.

326. $\text{HC}_2\text{H}_3\text{O}_2$. Acetic acid. To some of the dry salt in a test tube add equal volumes of alcohol ($\text{C}_2\text{H}_5\text{OH}$) and strong H_2SO_4 ; heat gently if necessary. The H_2SO_4 liberates $\text{HC}_2\text{H}_3\text{O}_2$, which reacts with the alcohol, forming ethyl acetate ($\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$); this may be recognized by its fruity odor.

Another test. — Some prefer the following test for acetic acid: The addition of *two drops* of $\text{FeCl}_3 + \text{Aq}$ to a cold neutral solution of an acetate turns the solution red from the formation of $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$; when this is boiled a brown basic salt is precipitated and the liquid becomes colorless. Groups III to VI of bases must be removed and the solution made strictly neutral, however, before this test can be applied.

327. Scheme for Acid Analysis. — The preliminary work on acids showed that if BaCl_2 produced a precipitate, Group I only was present; and if AgNO_3 in the presence of HNO_3 produced a precipitate, Group II only was present. The addition of HCl to the Group I precipitate, and of NH_4OH to the Group II precipitate, showed that each group might be further subdivided. In the analysis of an unknown solution for acids the method given in the following scheme will probably be found most convenient. In this connection reread section 301. Test for the acid radical in three unknown solutions containing one acid each. If the tests for acids in the unknown solutions do not come out satisfactorily, try blank tests on the known solutions of individual acids to find out the conditions necessary for conclusive reactions.

328.**Scheme for Group I of Acids**

Since in ordinary practice the substance to be tested for acids has already been examined for bases, the presence of Cr and As has been discovered ; if found, they may be present as H_2CrO_4 , H_3AsO_3 , and H_3AsO_4 ; the presence of these three acids must now be confirmed by their special tests applied to fresh portions of the original solution ; for the special tests for these acids see sections **303**, **304**, and **305** ; if these acids are present, the As and Cr must be removed by means of H_2S and $(\text{NH}_4)_2\text{S}$ before BaCl_2 is added to test for the other acids.

The presence of H_2SO_3 , $\text{H}_2\text{S}_2\text{O}_3$, and H_2CO_3 is determined by adding dilute HCl to a fresh portion of the original solution ; if present, these acids must be destroyed by adding HCl in slight excess and filtering off any precipitated sulphur.

To a solution free from H_2SO_3 , $\text{H}_2\text{S}_2\text{O}_3$, H_2CO_3 , H_2CrO_4 , H_3AsO_3 , and H_3AsO_4 add NH_4OH if necessary till neutral ; then add $\text{BaCl}_2 + \text{Aq}$.

P. Contains Ba salts of H_3PO_4 , H_3BO_3 , $\text{H}_2\text{C}_2\text{O}_4$, HF, H_4SiO_4 , $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, and H_2SO_4 ; add dilute HCl in excess.

If the **P.** dissolves ; H_2SO_4 is absent ; H_3PO_4 , H_3BO_3 , $\text{H}_2\text{C}_2\text{O}_4$, HF, H_4SiO_4 , or $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ is present. To the HCl solution add NH_4OH till slightly alkaline.

If the **P.** does not dissolve, H_2SO_4 is present and the other acids may be. In this case special tests for all the acids of Group I must be made in fresh portions of the original solution.

If no precipitate forms, H_3PO_4 and $\text{H}_2\text{C}_2\text{O}_4$ are absent and special tests should be applied to fresh portions of the original solution for H_3BO_3 , HF, H_4SiO_4 , and $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. See sections **309**, **311**, **314**, and **312**.

If a precipitate is formed, H_3PO_4 and $\text{H}_2\text{C}_2\text{O}_4$ are present and the other acids will probably stay in solution. In this case special tests for all the acids except H_2SO_4 must be made in fresh portions of the original solution.

If BaCl_2 gives a precipitate, it is often advisable to add $\text{CaCl}_2 + \text{Aq}$ to a fresh portion of the same solution to which BaCl_2 was added, but it should be rendered slightly alkaline with NH_4OH before adding CaCl_2 . A white precipitate shows H_3PO_4 , H_3BO_3 , $\text{H}_2\text{C}_2\text{O}_4$, HF, and $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ present ; also H_2SO_4 if the solution is concentrated. Add $\text{HC}_2\text{H}_3\text{O}_2$.

If the precipitate dissolves, $\text{H}_2\text{C}_2\text{O}_4$ and HF are absent ; H_3PO_4 , H_3BO_3 , and $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, present.

If the precipitate does not dissolve, HF and $\text{H}_2\text{C}_2\text{O}_4$ are present and the other three acids may be present.

In either case compare the results from CaCl_2 with the results from BaCl_2 before trying any special tests.

329.**Scheme for Group II of Acids**

The presence of H_2S has already been discovered by the addition of HCl in the basic analysis. If present, it must be destroyed by adding HNO_3 in excess to a fresh portion of the solution.

To a solution free from H_2S add HNO_3 to prevent the precipitation of acids of Group I, and then add AgNO_3 .

P. Contains the Ag salts of HCl , HBr , HI , HCN , $\text{H}_4\text{Fe}(\text{CN})_6$, and $\text{H}_6\text{Fe}_2(\text{CN})_{12}$. Add NH_4OH in considerable excess.

If the precipitate dissolves, HI and $\text{H}_4\text{Fe}(\text{CN})_6$ are absent. HCl , HBr , HCN , and $\text{H}_6\text{Fe}_2(\text{CN})_{12}$ are present, and special tests for these four acids must be made in some of the original solution.

If the precipitate does not dissolve, HI and $\text{H}_4\text{Fe}(\text{CN})_6$ are present; the other acids of the group may be present also. Special tests for all the acids of the group must then be made in some of the original solution.

In the absence of bromides, iodides, and cyanides, a precipitate with silver nitrate, soluble in aqua ammonia but insoluble in nitric acid, is sufficient test for a chloride. This method is simpler and more delicate than the special test for chloride; such tests must be applied, however, when other halogen acids are present.

330.**Scheme for Group III of Acids**

There is no general reagent for this group, and the special tests for HNO_3 , HClO_3 , and $\text{HC}_2\text{H}_3\text{O}_2$ must be tried in separate portions of the original solution.

PART IV

SALT ANALYSIS

331. Introduction. — In analyzing an unknown salt it is best to determine first the base present and then the acid radical. Before proceeding with this regular analysis, however, a little preliminary study of the general appearance of the substance will often give considerable information as to the probable composition of the substance and indicate which groups of bases need more careful attention. Occasionally the preliminary work determines a salt, but it is not safe to rely upon this alone, for negative results here do not always indicate the absence of certain bases or acids; in addition it should be remembered that some of the reactions are readily obtained and correctly interpreted only after considerable experience. Therefore too much time should not be spent on the preliminary analysis, and its results should always be verified by the basic and acid work.

332. The complete analysis of a salt is, therefore, divided into three parts: (*a*) preliminary analysis, (*b*) basic analysis, (*c*) acid analysis.

333. The preliminary analysis consists of these seven parts:

1. General properties.
2. Heating in bulb tube.
3. Heating on charcoal alone.
4. Heating on charcoal with Na_2CO_3 .
5. Borax bead.
6. Flame coloration.
7. Action with concentrated H_2SO_4 .

For the preliminary examination the substance, if solid, must be reduced to a fine powder, and only a small quantity of it should be used for each test. If the original substance is in

liquid form and it is desired to try the preliminary tests, a little of the liquid should be evaporated to dryness, and the residue, if any is left, should be powdered.

Scheme for Preliminary Analysis of Salts	
334.	1. General Properties
(a) General Appearance. (b) Color. (c) Luster. (d) Crystalline Form. (e) Any marked special property.	
335.	2. Heating in Bulb Tube °
OBSERVATION	INDICATION
(a) Fuses.	Salts of alkali metals or salts of alkaline-earth metals.
(b) Does not fuse, but changes color.	A black oxide or C from an organic substance.
(1) Residue black.	ZnO.
(2) Yellow when hot and white when cold.	PbO.
(3) Brown when hot but yellow when cold.	
(c) Water given off.	Water of crystallization.
(1) With fusion.	Water of composition.
(2) Without fusion.	Water mechanically inclosed.
(3) With decrepitation.	
(d) Sublimates.	Sulphur.
(1) Brown when hot but yellow when cold.	Ammonium salts.
(2) White.	Iodine compounds.
(3) Black, vapor violet.	Hg or As.
(4) Metallic.	
(e) Gas escapes.	Nitrates, chlorates, dioxides.
(1) O ₂ (glowing match).	Carbonates.
(2) CO ₂ (limewater).	S, or S compounds.
(3) SO ₂ (odor).	Nitrates or nitrites.
(4) NO ₂ (color and odor).	Chlorides.
(5) Cl ₂ (color and odor).	Bromides.
(6) Br ₂ (color and odor).	Iodides.
(7) I ₂ (color and odor).	

336. 3. Heating on Charcoal alone°

OBSERVATION	INDICATION
Salt deflagrates. Salt melts and runs into the charcoal. Infusible and incandescent.	Nitrates and chlorates. Salts of alkali metals. Salts of alkaline-earth metals, Zn, Al, or SiO_2 .

337. 4. Heating on Charcoal with Na_2CO_3 °

METALLIC GLOBULE	COATING HOT	COATING COLD	INDICATION
Malleable.	Orange-yellow.	Yellow.	Pb.
Malleable.	Pale yellow.	White.	Sn.
Malleable and bright.	No coating.	No coating.	Ag.
Malleable and red.	No coating.	No coating.	Cu.
Brittle.	Orange.	Yellow.	Bi.
Brittle.	White.	White.	Sb.

338. 5. Borax Bead°

OUTER FLAME		INNER FLAME		INDICATION
Hot	Cold	Hot	Cold	
Green.	Blue.	Colorless.	Red opaque.	Cu.
Blue.	Blue.	Blue.	Blue.	Co.
Violet.	Red-brown.	Gray.	Gray.	Ni.
Red.	Yellow.	Green.	Green.	Fe.
Violet.	Amethyst.	Colorless.	Colorless.	Mn.

339. 6. Flame Coloration°

COLOR	INDICATION	COLOR	INDICATION
Violet.	K.	Yellow.	Na.
Carmine.	Li.	Bright green.	Cu.
Crimson.	Sr.	Yellowish green.	Ba.
Orange.	Ca.	Pale blue.	Pb or As.

340. 7. Action with Concentrated H_2SO_4 °

OBSERVATION	INDICATION	OBSERVATION	INDICATION
ClO_2 (color and odor). HCl (odor). HBr or Br_2 (color). HI or I_2 (color). H_2S (odor).	Chlorates. Chlorides. Bromides. Iodides. Sulphides.	CO_2 (limewater). SO_2 (odor). S and SO_2 (odor). Blackens.	Carbonates. Sulphites. Thiosulphates. Tartrates ; and organic matter.

341. Notes on Scheme for Preliminary Analysis of Salts. — The following notes will be found of service in the preliminary analysis of the first few salts.

342. Heating in the Bulb Tube. — The bulb tube should preferably be of hard glass, though for many salts soft glass answers as well; the diameter of the bulb should not be much greater than the bore of the tube. Put enough of the finely powdered substance in the bulb tube nearly to fill the bulb; heat, gently at first, then to the highest heat of the Bunsen burner flame. Note any change of appearance and any odor. Organic matter generally emits a characteristic odor when it chars; if much organic matter is present, it must often be destroyed before the examination for bases is begun; this destruction may be accomplished by heating the substance till it is fully charred, or by heating it with a mixture of H_2SO_4 and HNO_3 . If water is present, it should always be reported; in order to detect it, keep the upper portion of the tube as cool as possible during the first part of the heating, so as to cause the moisture to condense; it may be present as water mechanically inclosed within the crystals; as hygroscopic moisture on the surface; as water of crystallization, as in $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$; or as water of composition, as in CaO_2H_2 or Na_2HPO_4 ; as the temperature is raised the different kinds of water generally come off in the order given above. The solid sublimate formed on the sides of the bulb tube should not be confounded with any of the original salt that may have stuck to the inside of the stem. Test for escaping oxygen by means of a glowing splinter of wood.

343. Heating on Charcoal Alone. — Dig out a little round hole in the charcoal with the handle end of the iron forceps, put a small amount of the dry substance in the hole, and heat in the inner or reducing flame of the blowpipe, directing the flame at an angle of about thirty degrees. Observe the odor evolved, also the nature of the residue in the cavity and of the coating if any. Many of the reactions of the bulb tube are repeated.

344. Heating on Charcoal with Na_2CO_3 . — Put a little of the dry substance in the cavity, cover with several times its volume of dry Na_2CO_3 , and heat with the blowpipe flame till the whole mass is fused. Let cool and look closely for the small metallic globules which should not be confounded with the residual lump of fused flux.

345. Borax Bead. — For detailed directions for making the borax bead test see section 115.

346. Flame Coloration. — For detailed directions for trying the flame coloration with the platinum test wire see sections 25 and 34. Hold the wire in the outer edge of the lower part of the Bunsen flame.

347. Action with Concentrated H_2SO_4 . — To a little of the powdered substance in a test tube add 3 or 4 c.c. of concentrated H_2SO_4 . If no reaction takes place in the cold, heat cautiously up to the boiling point of the H_2SO_4 . Note the color and odor of any gas evolved.

348. Preparation of the Solution. — After completing the preliminary examination of the solid substance, prepare a solution of it, and submit this to the systematic examination for bases and acids. A compound is either soluble in water, soluble in acids, or insoluble in both water and acids. In a mixture we may have compounds illustrating all of these phases of solubility. Hence it is necessary to determine if the substance presented for analysis can be separated into two or three parts according to these phases. If the mixture contains two or more substances, soluble in different solvents, the two solutions obtained, namely, of the part soluble in water, and of the part soluble in acids only, should be examined separately for bases and acids. If any portion of the mixture is insoluble in acids this should be examined by the special methods in sections 373 to 388.

349. Treatment with Water. — Put about one gram of the finely powdered substance in a large test tube, or a small beaker, add water, and bring to a boil. If the substance dissolves completely, examine this solution for bases and acids.

350. The aqueous solution should be tested with litmus paper. An alkaline reaction shows the presence of a soluble hydrate, carbonate, sulphide, phosphate, borate, or cyanide. An acid reaction shows the presence of a free acid, an acid salt of a strong acid, or a normal salt with acid reaction; in the first two cases a drop of $Na_2CO_3 + Aq$ gives no permanent precipitate; in the last case the turbidity is permanent.

351. Most salts are more readily soluble in hot water than in cold; in a few cases the reverse is true; and some salts, though

soluble in cold water, are decomposed by boiling water into insoluble basic salts. Salts of Bi and some salts of Sb and Hg are thus decomposed even by cold water.

352. If the original substance does not dissolve completely in water, filter a little of the liquid, and evaporate a few drops of the filtrate to dryness on a watch glass or platinum foil. No residue shows that the original substance was entirely insoluble; in that case decant the clear water and treat the residue with acids as directed in sections **354** to **363**.

353. A residue left on the watch glass shows either that the substance consisted of one compound that was sparingly soluble, or that it was a mixture, one part being soluble in water and the other insoluble. If partial solution takes place, allow the substance to settle out, decant, and boil the residue with a fresh portion of water to insure complete separation of the part soluble in water; filter; add the filtrate to the decantate and examine this solution for bases and acids. Treat the insoluble part as described in sections **354** to **363**.

354. Treatment with Acids.—For the solution of a substance insoluble in water, HCl alone, HNO₃ alone, or a mixture of the two as aqua regia may be used, but HCl is preferable.

355. To the substance found insoluble in water, or freed from any part soluble in water, add a little dilute HCl and heat. If complete solution takes place, use this solution for the regular basic and acid work. Note carefully if any effervescence or evolution of gas or odor takes place; HCl evolves CO₂ from carbonates, H₂S from sulphides, SO₂ from sulphites and thio-sulphates, HCN from cyanides, and Cl₂ in the presence of chlorates, chromates, or peroxides; S or H₄SiO₄ often separate.

356. If gelatinous H₄SiO₄ separates, or if a mineral containing a silicate is probably present, the HCl solution should be evaporated to dryness and the residue ignited carefully at low red heat for about an hour; the mass should then be dissolved in a little HCl, water added, and the solution filtered from the gritty SiO₂ and analyzed as usual for bases and acids. The silicic acid, which generally separates in hydrated, gelatinous

form and is then somewhat soluble in acids, is rendered anhydrous and insoluble by ignition.

357. If the substance does not dissolve completely in dilute HCl, decant and save the clear liquid; add a very little concentrated HCl to the residue and boil. If solution takes place, dilute with several volumes of water, add the resulting liquid to the other HCl solution, and examine for bases and acids. If concentrated HCl does not effect complete solution, dilute with several volumes of water; decant the clear liquid, add it to the HCl solution previously obtained, and test this for bases and acids. Many substances are soluble in dilute acids, but insoluble in strong; many are soluble in strong acids only; and again, many that are not attacked by dilute acids are decomposed, though not dissolved, by stronger acids so that solution can be effected only by treatment with strong acids and subsequent dilution with water.

358. Any residue left from the treatment with concentrated HCl should be treated with HNO_3 , first dilute and then concentrated, in just the same way that the original insoluble substance was treated with HCl. Combine all portions soluble in HNO_3 and examine this for bases and acids.

359. If the substance is a metal or an alloy, as will be indicated by the preliminary analysis, it should be treated at once with hot nitric acid — one part of concentrated acid to three parts of water — as long as any action continues. Sb and Sn are oxidized to Sb_2O_3 and SnO_2 , insoluble in water or dilute HNO_3 , and the other metals are found in solution as nitrates. The nitrates formed in dissolving the metal, though readily soluble in water, are only slightly soluble in strong HNO_3 ; they may therefore precipitate on the surface of the metal and prevent further action by the acid; care should be taken not to mistake the crystalline nitrates for the oxides of Sb and Sn. If an insoluble residue collects around the metal pour off the acid, treat the residue with water and then with a fresh portion of HNO_3 .

360. If the metal dissolves completely in HNO_3 , dilute with water and add HCl. Any precipitate formed is PbCl_2 or

AgCl; filter it off and test it for Pb and Ag as in the Group V work. Evaporate the filtrate, or the solution in which HCl gave no precipitate, to dryness; moisten the residue with HCl and evaporate just to dryness to expel the free HNO_3 . Dissolve the residue in water, using a few drops of HCl if necessary; pass in H_2S and proceed with the regular basic analysis. The treatment of the H_2S precipitate with yellow $(\text{NH}_4)_2\text{S}_2$ for Group VI may, however, be omitted, because As, Sb, and Sn are usually absent when the metal dissolves completely in nitric acid.

361. If the metal does not dissolve completely in HNO_3 , and a white residue is left, dilute the HNO_3 solution with water, filter, and examine the filtrate as described in section 360. Wash the residue with hot water till free from acid, add some yellow $(\text{NH}_4)_2\text{S}_2$, and heat. The white residue should dissolve entirely; if any small amount of residue remains, filter it off and examine the $(\text{NH}_4)_2\text{S}_2$ solution for As, Sb, and Sn in the usual way. If the white residue does not dissolve readily in yellow $(\text{NH}_4)_2\text{S}_2$, dissolve a fresh portion of the metal with aqua regia, and proceed with this solution as with the HNO_3 solution; but include the examination for Group VI.

362. If neither HCl nor HNO_3 effects complete solution, the insoluble substance, or the residue left after treatment with HCl and HNO_3 , must be treated with hot aqua regia — a mixture of three parts of concentrated HCl and one part of concentrated HNO_3 . Use as little aqua regia as possible, as any large excess of acid must be expelled by evaporation before H_2S can be passed in. Dilute with several volumes of water and analyze for bases and acids. Aqua regia dissolves by converting the metals into the chlorides. Any insoluble residue left by aqua regia must be examined by the method for insolubles in sections 373 to 388.

363. When sulphides are dissolved in HNO_3 or aqua regia, sulphur often separates in the form of a light spongy mass, sometimes black at first owing to inclosed matter, but becoming yellow on continued boiling; it may be tested by heating on porcelain, when it burns with a blue flame and an odor of SO_2 .

364. The directions given in sections **354** to **363** for the preparation of the solution are here condensed in the following table:

Preparation of the Solution				
Boil about 1 gram of the substance with water ; allow the insoluble portion to settle ; filter.				
Filtrate. Label this Solution W and examine it for bases and acids.	Residue. Boil with dilute HCl ; allow the insoluble portion to settle ; filter.			
	Filtrate.	Residue. Boil with concentrated HCl ; dilute ; allow the insoluble portion to settle ; filter.		
		Filtrate.	Residue. Boil with dilute HNO ₃ ; add water ; allow the insoluble portion to settle ; filter.	
	Combine these two filtrates ; evaporate if too bulky or too acid ; label it Solution A₁ and examine it for bases and acids.		Filtrate.	Residue. Boil with concentrated HNO ₃ ; dilute with water ; allow the insoluble portion to settle ; filter.
			Filtrate.	Residue. Warm with aqua regia ; dilute with water ; allow the insoluble portion to settle ; filter.
	Combine these two filtrates ; evaporate to expel excess of HNO ₃ ; label it Solution A₂ and examine it for bases and acids.		Combine these two filtrates ; evaporate to expel excess of HNO ₃ ; label it Solution A₂ and examine it for bases and acids.	Filtrate. Evaporate nearly to dryness ; dilute with water ; label it Solution A₃ and examine it for bases and acids.

365. The **acid analysis** of substances soluble in acids only may be greatly simplified by noting carefully the action of the solid with the acids that dissolve it. In this way many salts, such as carbonates, sulphides, etc., are easily recognized.

366. The nature of the base taken in connection with the solubility of the salt often limits the number of acids that need to be looked for.

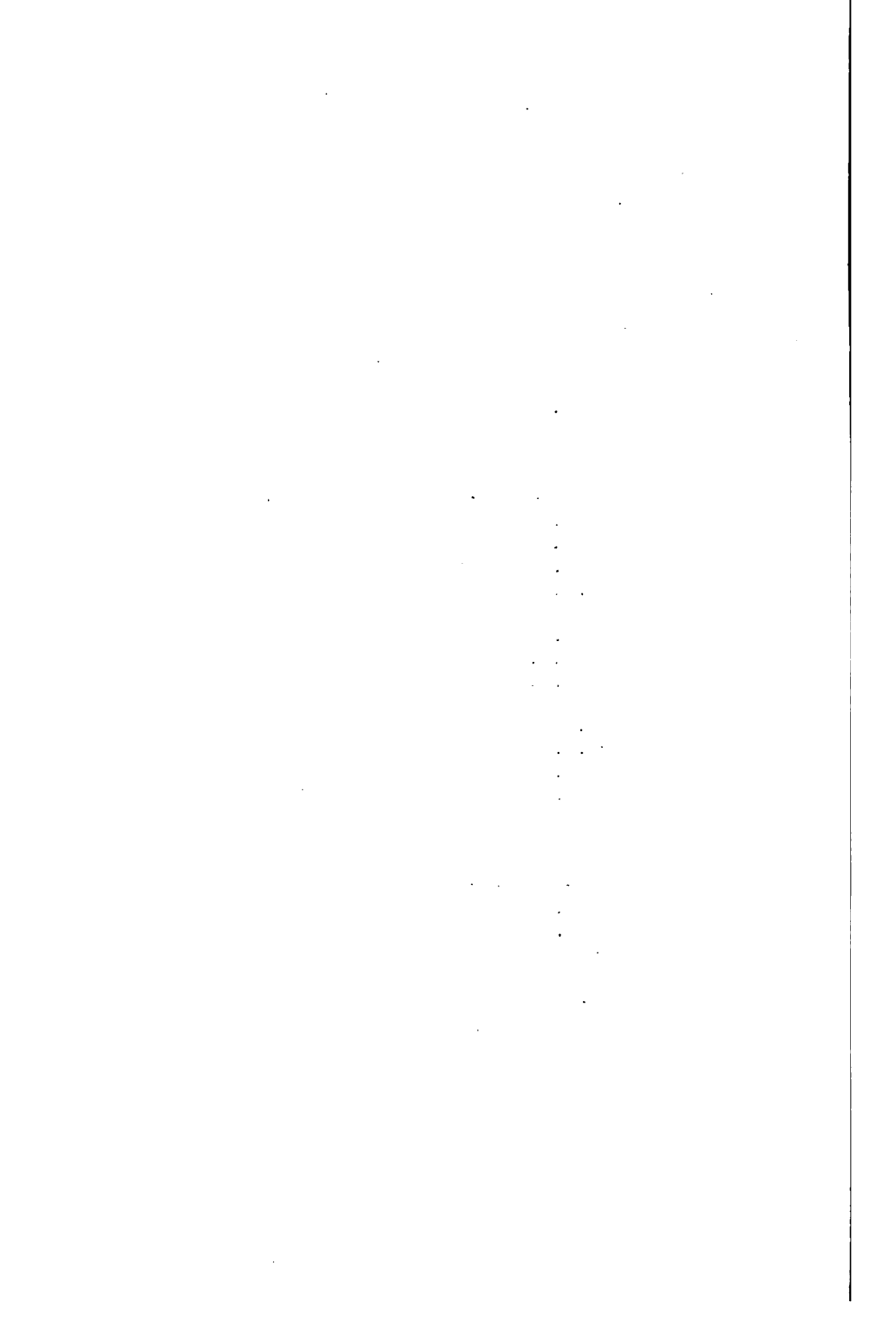
367. If the salt is soluble in water and only alkali and alkaline-earth metals are present, the tests for acids may be made in the aqueous solution of the salt.

368. If the salt is soluble in water and other metals are present, it is not necessary to look for acids that with these metals form insoluble compounds; the metals must, however, be removed before testing for those acids that may be present, because they interfere with some of the special tests; this is done by adding $\text{Na}_2\text{CO}_3 + \text{Aq}$ to the solution as long as a precipitate forms, and filtering off the precipitate. All metals except As and the alkalies are precipitated from solution by Na_2CO_3 in the form of carbonate or hydrate.

369. If the salt is insoluble in water and metals not precipitated by H_2S are present, boil about 1 gram of the powdered salt with 10 c.c. of strong Na_2CO_3 solution for ten or fifteen minutes, replacing the water which evaporates. Boiling with Na_2CO_3 decomposes almost all salts more or less completely, the acid radical going into solution in combination with sodium, and the metal being precipitated as the carbonate or hydrate. Filter off the precipitate and make half the filtrate slightly acid with HNO_3 . If any precipitate forms when the solution is nearly neutral, filter it off and throw it away; this precipitate consists of traces of the carbonates and hydrates that dissolved in the excess of Na_2CO_3 . Boil the HNO_3 solution a few minutes to expel the CO_2 and use it for the BaCl_2 and AgNO_3 tests and for those special tests which may be made in the presence of free HNO_3 ; if the CO_2 is not expelled, BaCO_3 and Ag_2CO_3 are likely to come down. Acidify fresh portions of the Na_2CO_3

luble in water ; readily soluble in acids.
 luble in water ; sparingly soluble in acids.
 water ; sparingly soluble in acids.

Cu	Cd	Bi	As	Sb	Sn(ous)	Sn(ic)	
W	A	A	—	A	A	A-I	H ₂ CrO ₄
A	—	—	—	A	—	—	H ₃ AsO ₃
A	—	A	—	A	—	A	H ₃ AsO ₄
W-A	W-A	A	—	A	W-A	—	H ₂ SO ₃
W-A	W	—	—	—	—	—	H ₂ S ₂ O ₃
A	A	A	A	W-A	A	A	H ₃ PO ₄
A	W-A	A	—	—	A	—	H ₃ BO ₃
A	A	A	—	A	A	W	H ₂ C ₂ O ₄
A	W-A	W	W	W	W	W	HF
W	W-A	A	—	A	A	—	H ₂ C ₄ H ₄ O ₆
A	A	A	—	—	—	—	H ₂ CO ₃
A	A	—	—	—	—	—	H ₂ SiO ₃
W	W	W	—	A	W	—	H ₂ SO ₄
W	W	W-A	W	W-A	W	W	HCl
W	W	W-A	W	W-A	—	—	HBr
W	W	A	W	W-A	W	W	HI
A	A	—	—	—	—	—	HCN
I	—	—	—	—	I	I	H ₄ Fe(CN) ₆
—	—	—	—	—	I	—	H ₆ Fe ₂ (CN) ₁₂
A	A	A	A	A	A	A	H ₂ S
W	W	W	—	—	—	—	HNO ₃
W	W	W	—	—	W	—	HClO ₃
W	W	W	—	—	W	W	HC ₂ H ₃ O ₂
A	A	A	A	A	A	A	Metal
A	A	A	A	A	A	A-I	Oxide
A	A	A	—	—	A	A	Hydrate



solution with $\text{HC}_2\text{H}_3\text{O}_2$ for the oxalic acid test, and with H_2SO_4 for the nitric acid test.

370. If the salt is insoluble in water and only metals precipitated by H_2S are present, suspend a little of the powdered salt in water, saturate with H_2S , heat to boiling, and filter. The removal of the metals with H_2S is more complete than with Na_2CO_3 , but it is of more limited application; in the presence of chlorates, too, it cannot be used, for the H_2S is oxidized and the tests for H_2SO_4 , HClO_3 , and HCl are valueless. Boil the filtrate till the H_2S is all expelled and use it for the BaCl_2 and AgNO_3 tests and for such special tests as it may be necessary to try.

371. Table of Solubilities. — In many cases it is not necessary to try the tests for all the acids. If the salt is soluble in water and only alkali metals are present, all acids must be looked for, because all salts of these metals are soluble in water. If the salt is soluble in water and other metals are present, it is not necessary to look for acids that with these metals form insoluble compounds. If the salt is insoluble in water and the base has been determined, it is not necessary to look for acids that with the metal in question form soluble salts. The Table of Solubilities in the next section gives the solubility in water and acids of the substances commonly found in inorganic chemical analysis, arranged to show the division into groups for both bases and acids. This table should always be consulted after the basic analysis has been completed and before the acid analysis is begun. To use the table look for the base, *e.g.* Mg , at the top and for the acid, *e.g.* H_2CO_3 , at either side. Opposite the acid and under the base will be found the letter, in this case A, that indicates the solubility.

373. Treatment of Substances Insoluble in Water and Acids. — If the substance under examination does not dissolve in water or acids, it must be decomposed and converted into other compounds capable of solution and subsequent analysis.

374. The most common substances insoluble in water or acids are: some ferrocyanides and ferricyanides; PbSO_4 ; C

and S; AgCl, AgBr, and AgI; BaSO₄, SrSO₄, and CaSO₄; CaF₂; ignited Al₂O₃, Cr₂O₃, Fe₃O₄, and SnO₂; SiO₂ and many native silicates; and minerals other than silicates, partially or not at all decomposed by previous treatment. The presence of some of these substances will probably have been indicated by the preliminary analysis.

375. An insoluble substance is generally subjected to the following treatment: boiling with strong sodium hydrate solution; special tests for and removal of C, S, PbSO₄, AgCl, AgBr, and AgI; fusion with sodium carbonate; and fusion with acid potassium sulphate.

376. Boiling with Sodium Hydrate.—Some substances insoluble, or slightly soluble, in acids may be decomposed to advantage by boiling with a strong solution of sodium hydrate. The insoluble ferrocyanides and ferricyanides are thus decomposed into sodium salts of the cyanogen acids and hydrates of the metals. Dilute the resulting liquid with water and filter. Dissolve the residue in HCl or HNO₃ and examine for bases. Neutralize the filtrate and test for acids; the filtrate should be examined for Al, Zn, and Pb also, and these, if found, should be removed before the tests for acids are made. If the residue from the treatment with NaOH does not dissolve in acids, dry it and try further tests for insolubles.

377. Special Tests before Fusion.—Special tests for S, C, PbSO₄, AgCl, AgBr, and AgI should be tried, and these substances removed, before proceeding to the fusion tests, because fusion may thereby be found unnecessary, or, if necessary, it may then be made in platinum crucibles.

378. S and C will have been recognized in the preliminary work,—S by the blue flame and the odor of SO₂, and C if the substance was black and part of it burned before the blowpipe. Ignite the substance in a porcelain crucible till the S and C are entirely expelled.

379. Any residue left after expelling the S and C must be tested for PbSO₄. Heat the residue with a strong solution of NH₄C₂H₃O₂ acidified with a few drops of HC₂H₃O₂; the PbSO₄

is dissolved. Filter and halve the filtrate ; in one part test for Pb by adding a few drops of $(\text{NH}_4)_2\text{S}$, and in the other, test for H_2SO_4 by adding a little BaCl_2 . Repeat the treatment with $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ till the PbSO_4 has all been dissolved out.

380. Any residue left after the removal of PbSO_4 must be tested for the halogen salts of Ag. Heat most of the residue with a strong KCN solution ; the Ag halide is dissolved. Filter, and add $(\text{NH}_4)_2\text{S}$ to the filtrate ; a black precipitate of Ag_2S shows the presence of Ag. If Ag is present, put the rest of the residue in a porcelain crucible, add metallic Zn and dilute H_2SO_4 , and allow the action to continue for at least fifteen minutes. The halide of Ag is reduced by this treatment, the Ag separating in metallic form and the halogen acid being set free. Filter from the Ag and excess of Zn, precipitate the Zn in the filtrate with an excess of Na_2CO_3 , and test in the resulting liquid for HCl, HBr, and HI. If KCN did not effect complete solution, repeat the treatment with KCN solution till all the Ag salt is dissolved out.

381. Fusion with Sodium Carbonate.—Any residue left after the removal of the Ag salts by the KCN treatment is likely to contain BaSO_4 , SrSO_4 , and CaSO_4 ; CaF_2 ; ignited Al_2O_3 , Cr_2O_3 , Fe_3O_4 , and SnO_2 ; SiO_2 and silicates ; and possibly some minerals not decomposed by previous treatment. This residue must now be subjected to the fusion tests. If Ag and Pb have been removed completely, the fusion may be done in a platinum crucible ; if not, a porcelain crucible must be used ; for platinum is affected by Ag, Pb, and other reducible metals such as Cu, Hg, As, Sb, and Bi ; it is also spoiled by fusion with sulphides, or with phosphates in the presence of organic matter. In the last case porcelain must be used, but then Al and SiO_2 cannot be tested for in the fused mass, for Na_2CO_3 attacks porcelain. Platinum is preferable, however, wherever it can be used, because the required high temperature is more easily attained with platinum than with porcelain.

382. Mix the dry, insoluble residue with five or six times its weight of flux ; this generally consists of equal parts of

Na_2CO_3 and K_2CO_3 , but a little KNO_3 may be added if the fusion does not take place readily. Not too much of the substance should be taken, and the mixture should not fill the crucible more than two thirds full. Use a platinum crucible if allowable, otherwise porcelain. Fuse the mixture to a thin liquid, applying the heat gently at first, then the full heat of the Bunsen, and finally the blast lamp, if necessary. Continue the heating ten or fifteen minutes, or longer if effervescence has not ceased. While the fused mass is still hot and liquid, quickly pour it out on an unglazed porcelain surface. When the mass has cooled, break it into bits and boil with water till it is entirely disintegrated, replacing the water as it evaporates. Filter and wash the residue till free from Na_2CO_3 .

383. During the fusion the Na_2CO_3 decomposes most substances, the acid radical of the compound combining with the Na, while the carbonate of the metal is formed, if this is stable at high temperature; otherwise the oxide, or possibly the metal itself, is formed. The acid radical of the original compound is found in the aqueous solution of the fused mass, and the metal is found in the residue from the treatment with water.

384. A small portion of the residue from the treatment of the fused mass with water should be dissolved in dilute HNO_3 , and this solution should be tested for Ag and Pb. The rest of the residue should be dissolved in dilute HCl. To a little of this HCl solution add a little of the aqueous solution of the fused mass, and make the mixture acid with HCl if it is not so already. If no precipitate forms, save half of the aqueous solution for the tests for acids, and mix the other half with the acid solution of the fusion; if it is alkaline, make acid with HCl, evaporate carefully to dryness, and bake for about a half an hour on a ring over an iron plate to render the silica insoluble; moisten with HCl, boil out with water, and filter from the residue, which contains SiO_2 and any substance unchanged by the fusion. Test the filtrate for bases by the regular procedure.

385. If the fused substance turns out to be a natural silicate, the filtrate will not give the tests for the alkali metals, for

alkali silicates, though soluble in water when present alone, are insoluble, even in acids, when present in double silicates. In such a case the mineral must be decomposed without the use of an alkaline carbonate. Fuse a little of the powdered substance with four parts of barium hydrate. Disintegrate the fused mass by boiling with water, and filter. Remove the excess of barium in the hot filtrate by means of dilute H_2SO_4 , evaporate the filtrate to dryness, expel the excess of H_2SO_4 , and test for Na, K, and Li.

386. The residue from boiling the Na_2CO_3 fusion with water contains SiO_2 and substances unchanged by the fusion. Treat it in a platinum crucible with a few c.c. of HF; evaporate off the excess of HF carefully. If nothing remains, it shows the residue was SiO_2 ; HF decomposes SiO_2 and silicates, forming gaseous silicon tetrafluoride, SiF_4 , which passes off.

387. Fusion with Acid Potassium Sulphate.—If a residue remains after the treatment with HF, it is probably Al_2O_3 , Cr_2O_3 , and Fe_3O_4 . Mix it with five parts of KHSO_4 and heat to quiet fusion, but not till fumes of acid cease. The metals are converted into soluble sulphates, and the SiO_2 , if any silicate is present, separates in insoluble form. If the mass is heated till the H_2SO_4 fumes cease coming off, the sulphates are changed to insoluble basic sulphates. Disintegrate the fused mass by boiling with water, filter off the residue, and examine the filtrate for bases.

388. The three portions of any substance—that soluble in water, that soluble in acids only, and that insoluble in water and acids—must be analyzed separately. The larger portion should be examined first, because a knowledge of its composition may throw considerable light on the probable composition of the other portions, thereby making the analysis of these portions easier. As far as possible, too, the analysis should show the relative amounts of the different portions.

389. The student should run through the analysis of a few known salts and verify all the reactions, being careful to write up a good account covering all the steps.

390. Sample Page from Laboratory Notebook. — In order to save time in writing up the notes on unknown salts, it is well to use any condensed form that will show all the essential steps in the analysis with all the results that show the presence or absence of a base or an acid. The following sample page from a laboratory notebook is given merely as a suggestion and need not be followed exactly if the student prefers some other form which is as clear. The abbreviations under the preliminary analysis refer to the parts of the Scheme for Preliminary Work.

Salt No. 000	
Prelim.	
Gen. Prop.	glassy lumps; slightly efflorescent.
B. T.	fuses; dark residue with odor; probably an organic substance.
Ch.	fuses and runs in.
Ch+	fuses and runs in; flares up.
Fl.	yellow; Na.
Bx. Bd.	nothing.
H ₂ O	soluble.
H ₂ SO ₄	gas evolved; has odor (?).
Basic	
HCl, H ₂ S	nothing; Gr. V and VI abs.
NH ₄ Cl, NH ₄ OH, (NH ₄) ₂ S	nothing; Gr. III and IV abs.
(NH ₄) ₂ CO ₃	nothing; Ba, Ca, Sr abs.
Na ₂ HPO ₄	nothing; Mg abs.
Flame	yellow; Na pres. K and Li abs.
CaO ₂ H ₂	nothing; NH ₄ abs.
Acid	
Basic work shows Cr and As abs.	HCl shows H ₂ SO ₃ , H ₂ S ₂ O ₃ , H ₂ CO ₃ , and H ₂ S abs.
BaCl ₂	nothing; Gr. I abs.
AgNO ₃	nothing; Gr. II abs.
FeSO ₄ , H ₂ SO ₄	nothing; HNO ₃ abs.
Prelim.	shows HClO ₃ abs.
C ₂ H ₅ OH, H ₂ SO ₄	characteristic odor. HC ₂ H ₃ O ₂ pres.
∴ NaC ₂ H ₃ O ₂ present.	

PART V

APPENDIX

COLLATERAL READING

391. Since this little book is strictly a laboratory manual, all descriptive and theoretical matter has been omitted. Some outside reading on these portions will increase the student's grasp of the subject. The following list indicates a few of the books that may be used to advantage in such collateral reading and for general reference:

Fresenius, Manual of Qualitative Chemical Analysis. Translated by H. L. Wells. 748 pages. John Wiley and Sons. Very full. For many years the standard authority on qualitative analysis. Valuable as a reference book for teachers and advanced students. No equations.

Treadwell, Analytical Chemistry, Volume I, Qualitative Analysis. Translated by W. T. Hall. 466 pages. John Wiley and Sons. Very full and up-to-date. Particularly good on preliminary work. Equations given in full, many of them graphically. Splendid reference book for students.

Prescott and Johnson, Qualitative Chemical Analysis. 420 pages. D. Van Nostrand Company. Very full. Suitable for general reference.

Hill, Lecture Notes on Qualitative Analysis. 54 pages. G. P. Putnam's Sons. Concise laboratory manual.

Noyes, A. A., Qualitative Chemical Analysis. 89 pages. The Macmillan Co. Text arranged under Procedure, Notes, and Outline of the process. Very clear. Many reasons and precautions are given. The directions for the preparation

of the solution for the analysis for metals and for acids are particularly good. Has good treatment, in three pages, of oxidation and reduction, and the best method for balancing equations involving these changes.

Biedermann, Chemiker-Kalender. 362 pages. Julius Springer of Berlin. Contains sixteen pages of very full and valuable tables of preliminary work for bases and acids. In German.

Noyes, W. A., The Elements of Qualitative Analysis. 101 pages. Henry Holt and Co. Contains fourteen pages of tables giving in English much of the substance of the tables mentioned under Biedermann's Chemiker-Kalender.

Ostwald, Scientific Foundations of Analytical Chemistry. Translated by McGowan. 215 pages. The Macmillan Co. Good treatment of modern theoretical conceptions of analytical reactions.

Talbot and Blanchard, The Electrolytic Dissociation Theory and Some of its Applications. 84 pages. The Macmillan Co. An elementary treatise for the use of students of chemistry. A valuable reference book for both student and teacher.

Böttger, The Principles of Qualitative Analysis. Translated by Smeaton. 300 pages. P. Blakiston's Son and Co. Written from the standpoint of the theory of electrolytic dissociation and the law of mass action. Up-to-date. Valuable for reference.

Dennis and Whittelsey, Qualitative Analysis. 142 pages. Ginn and Co. Gives, in four pages, a good presentation of the method of balancing equations.

Newth, A Manual of Chemical Analysis, Qualitative and Quantitative. 472 pages. Longmans, Green, and Co. Illustrated. 188 pages are devoted to Qualitative Analysis. Regarded by many as the best brief treatment in a single book of both phases of analytical chemistry.

Comey, A Dictionary of Chemical Solubilities (Inorganic). 515 pages. The Macmillan Co. Very full. Until recently practically the only reference work on solubilities outside of the brief tables found in some text-books on qualitative analysis.

Seidell, Solubilities of Inorganic and Organic Substances. 380 pages. D. Van Nostrand Co. Contains the solubilities of both organic and inorganic substances, not only in water, but also in the other common solvents, and in many cases in salt or other solutions as well. Many determinations have been recalculated to a common basis, and the most reliable values selected.

Richter, Text-book of Inorganic Chemistry. Edited by Klinger. Translated by Smith. 430 pages. P. Blakiston's Son and Co. Splendid reference book on General Descriptive Inorganic Chemistry. Theory treated briefly but clearly.

Watts, Dictionary of Chemistry. Edited by Morley and Muir. 4 volumes. Total number of pages 3290. Longmans, Green and Co. Described by the Text-Book Committee of the New England Association of Chemistry Teachers, as: "Voluminous, comprehensive, and authoritative. The best available reference book covering the whole subject. Probably will not be replaced for many years."

DIVISION OF WORK IN QUALITATIVE ANALYSIS

392. Several years' experience with the manuscript of this book has shown that the work outlined in these pages can occupy with profit twenty-seven weeks. This covers: (1) the preliminary work on each group of bases and of acids, (2) the analysis of a known solution on each group, (3) the analysis of twenty-five unknown solutions for bases and three unknown solutions for acid radicals, and (4) the complete analysis of twenty salts.

393. The following table shows how much work the student should cover each week:

NUMBER
OF
WEEK

Work to be Done

1. Introduction.

Preliminary Work for Group I.

Group I, Known Solution.

Group I, Unknown Solutions (Solutions 1, 2, 3).

NUMBER
OF
WEEK**Work to be Done**

2. Preliminary Work for Group II.
3. Scheme for Group II.
Group II, Known Solution.
Group II, Unknown Solutions (Solutions 4, 5, 6).
4. Scheme for Groups I and II.
Groups I and II, Unknown Solutions (Solutions 7, 8, 9).
5. Preliminary Work for Groups III and IV.
6. Scheme for Groups III and IV.
Groups III and IV, Known Solution.
7. Groups III and IV, Unknown Solutions (Solutions 10, 11, 12).
8. Scheme for Groups I to IV.
Groups I to IV, Unknown Solutions (Solutions 13, 14, 15).
9. Preliminary Work for Group V.
10. Scheme for Group V.
Group V, Known Solution.
11. Group V, Unknown Solutions (Solutions 16, 17, 18).
12. Scheme for Groups I to V.
Groups I to V, Unknown Solutions (Solutions 19, 20, 21).
13. Preliminary Work for Group VI.
14. Scheme for Group VI.
Group VI, Known Solution.
Group VI, Unknown Solutions (Solutions 22, 23, 24).
15. Scheme for Groups I to VI.
Groups I to VI, Unknown Solutions (Solution 25).
16. Grouping of Acids.
Preliminary Work on Acids.
Special Tests for Acids.
17. Scheme for Acid Analysis.
Unknown Acid Solutions (Solutions 26, 27, 28).
Table of Preliminary Analysis of Salts, with experimental selections from the Preliminary Analysis Tables.

NUMBER
OF
WEEK**Work to be Done**

18. Complete Analysis of one or two unknown salts.
Laboratory Notebook Record of analysis of unknown salt.
Use of Table of Solubilities.
Unknown Salts 1, 2.
19. Method of Procedure for Insoluble Salts and for Alloys.
Unknown Salts 3, 4.
20. Unknown Salts 5, 6.
21. Unknown Salts 7, 8.
22. Unknown Salts 9, 10.
23. Unknown Salts 11, 12.
24. Unknown Salts 13, 14.
25. Unknown Salts 15, 16.
26. Unknown Salts 17, 18.
27. Unknown Salts 19, 20.

STUDY QUESTIONS

394. These questions are designed to furnish suggestions for a thoughtful consideration of work done at the laboratory desk, with special reference to the reasons for the different steps in the schemes of analysis.

395. Introduction. — What is Qualitative Analysis? Who was called "The Father of Qualitative Analysis"? Why was he so called? What is a reaction? What two kinds of reactions are there? Give an example of each. What is meant by a "reagent"? What two kinds of reagents are there? Define each. What is meant by "decantation"? By "filtration"? Define "decantate" and "filtrate." State Berthollet's Laws. Give the formula and name for each of the nineteen individual reagents.

396. Group I of Bases. — Give the name and symbol of each of the four members of Group I of Bases. Which members are called the alkali metals? Why are they so called? What color is imparted to a Bunsen flame by a salt of sodium? By a salt of potassium? By a salt of lithium? Which flame coloration

lasts longest? Which shortest? What is the easiest way to clean a platinum test wire if you are not in a hurry? If you are in a hurry? Explain fully the use of the cobalt glass and upon what property of the glass its use depends. If the glass is too thin, what mistake are you in danger of making when reporting on a solution containing lithium or sodium?

Why is not the flame test used for ammonium? Describe the test for ammonium in full. What precaution must be taken in the test for ammonium? Write the equation for the reaction between ammonium chloride and calcium hydrate. If a perfectly clean platinum wire be rubbed between the fingers, it will then give a yellow flame coloration; explain this. Under what conditions would you report only a trace of sodium present in an unknown solution? If you get a flame coloration that shows through the cobalt glass and you are not quite satisfied that potassium is present, what is the best thing to do? What is meant by a "blank test"?

397. Group II of Bases. — Give the name and symbol of each of the four members of Group II of Bases. Which members are called the alkaline-earth metals? Why are they so called? Why is magnesium grouped with the alkaline-earth metals in its qualitative study? What color is imparted to a Bunsen flame by a salt of barium? By a salt of strontium? By a salt of calcium? By a pure salt of magnesium? Which Group II metal might be confounded with a Group I metal, judging from the flame coloration alone?

What is the prevailing color of the precipitates obtained in the preliminary work on Group II? Which precipitate has a distinct color? Write the formulæ for calcium sulphate, barium sulphate, and strontium sulphate in the order of their solubility in water, beginning with the one that is the least soluble in water. What is the formula for calcium carbonate? What is the formula for basic magnesium carbonate? Write the equation for precipitating MgO_2H_2 . For precipitating MgCO_3 - MgO_2H_2 . Write the equations for precipitating barium carbonate, strontium carbonate, and calcium carbonate from solu-

tions of the chlorides. Write the equations for precipitating barium sulphate, calcium sulphate, and strontium sulphate from solutions of the chlorides by means of dilute sulphuric acid. Write the equations for precipitating barium sulphate and strontium sulphate from solutions of the chlorides by means of ammonium sulphate solution. Write the equation for making BaCrO_4 . Write the equations for precipitating the oxalates of barium, of strontium, and of calcium. Write the equations for precipitating BaHPO_4 , SrHPO_4 , CaHPO_4 , and MgHPO_4 . What is the solubility in hydrochloric acid of the carbonates of Group II? Of the phosphates? Of the oxalates? Of the sulphates?

In starting an unknown solution on Group II why add ammonium chloride? Why add ammonium hydrate? Why add ammonium carbonate? Why must the solution be heated almost to boiling before adding ammonium carbonate, and why must it not be actually boiled? How can you tell when ammonium carbonate has caused complete precipitation? Why should a large excess of nitric acid be avoided when dissolving the precipitated carbonates on the filter paper? Why must the nitrates of Ba, Sr, and Ca be heated until perfectly dry? Why must too high a temperature be avoided? What precaution must be taken when making the ether-alcohol mixture? Why must the nitrates of Ba and Sr be washed with ether-alcohol mixture till the filtrate gives no precipitate with H_2SO_4 ? Why must the solution containing Ba and Sr be diluted before removing the Ba? What reagent is added to remove the Ba? Why add ammonium sulphate to some of the filtrate supposed to contain Mg? Why add ammonium oxalate to some of the same filtrate? How are traces of Ba and Ca removed from the solution before testing for Mg? Describe the test for magnesium. In what respect is magnesium ammonium phosphate different from other white precipitates?

398. Groups I and II of Bases.—If to a solution containing all the members of Group II and of Group I we add NH_4Cl , NH_4OH , and $(\text{NH}_4)_2\text{CO}_3$, a precipitate is formed; what three metals are found in this precipitate? What five metals remain

in the filtrate from this precipitate? Why is it best to remove magnesium before testing for Group I? How is it removed? Why is it necessary to expel the ammonium salts by ignition before removing the magnesium?

An unknown solution on Groups I and II is found to contain Ba, Na, and Li, the nitrates being used in making up the solution. Give the names and formulæ for the six compounds dissolved in the filtrate from the precipitated barium carbonate.

An unknown solution is found to contain Ba, Sr, Ca, Na, Li, and K. Mg is absent. To what solution is the test for NH_4 applied? Why? Another solution is found to contain the same things present as before, but Mg also is present. To what solution is the test for NH_4 applied in this case? Why?

399. Groups III and IV of Bases. — Give the name and symbol of each of the two members of Group III of Bases. Give the name and symbol of each of the five members of Group IV of Bases. Why are these two groups considered together instead of separately? In what two states does iron exist? What is the valence of iron in ferrous compounds? What is the valence of ferric iron? What is the valence of aluminium? Of chromium? What is the valence of cobalt? Of nickel? Of manganese? Of zinc?

Give the formula and color of the hydrate of each member of Groups III and IV. Which of the hydrates are soluble in sodium hydrate solution? Which of the precipitated hydrates are soluble in ammonium hydrate solution? If ammonium chloride be added to separate solutions of the members of Groups III and IV, and then ammonium hydrate be added, which members will not give a precipitate on account of the presence of ammonium chloride? What is the general consistency of all the precipitated hydrates of these two groups?

What compound does ammonium sulphide precipitate from an aluminium solution? From a chromium solution? From an iron solution? From a cobalt solution? From a nickel solution? From a manganese solution? From a zinc solution?

What difference is there in the black precipitates thrown out by ammonium sulphide from a ferrous solution and from a ferric solution? Which two sulphides of Group IV are insoluble in dilute hydrochloric acid? Why does not hydrogen sulphide produce a precipitate in an aluminium solution? In a chromium solution? In a ferrous solution when an acid is present? What is the action of hydrogen sulphide on a ferric solution and what elementary substance separates? Must the solution be acid, neutral, or alkaline in order to produce a precipitate with hydrogen sulphide in a cobalt solution? Does the same hold true for nickel, manganese, and zinc solutions?

With which members of Groups III and IV will barium carbonate emulsion react, giving a precipitate? Give the formulæ for the precipitates formed by barium carbonate emulsion.

In what two states of oxidation does iron exist? Give the formula for a characteristic ferrous compound. For the corresponding ferric compound. What happens to a ferrous solution as it stands exposed to air? What is the color of ferrous sulphate solution? Of ferric sulphate solution? Which is more soluble in water, ferrous sulphate or ferric sulphate? What happens to a ferrous sulphate solution when it is boiled? How may a cloudy ferric sulphate solution be reduced to a ferrous sulphate solution? Write the equation for reducing ferric sulphate to ferrous sulphate by means of nascent hydrogen. Why is nitric acid a good oxidizing agent? How may a ferrous sulphate solution be oxidized to ferric sulphate? Write the equation for oxidizing ferrous sulphate to ferric sulphate by means of nitric acid.

What is the formula for potassium ferrocyanide? For potassium ferricyanide? For potassium sulphocyanide? Give the chemical name, the formula, and the color of Prussian blue. Of Turnbull's blue. What is the solubility of these two precipitates in hydrochloric acid? What color is always produced by potassium sulphocyanide in a ferric solution? Why is the same color often obtained on a small scale when potassium

sulphocyanide is added to a ferrous solution? What is the test for ferrous iron? For ferric iron? What is the best test for a minute trace of ferric iron?

In starting an unknown solution on Groups III and IV why add ammonium chloride? Why add ammonium hydrate till slightly alkaline? Why add ammonium sulphide? Why use a flask? In what respect do the precipitated sulphides of these two groups differ from the precipitated carbonates of Group II? If ammonium hydrate causes a precipitate, which metal does this precipitate indicate if it is white? If it is green? If it is greenish or red-brown? If ammonium hydrate gives no precipitate in the original solution, what three metals are thereby shown 'absent'? How may precipitation with ammonium sulphide be shown to be complete? Why must the ammonium sulphide be colorless or nearly so? How may the precipitate produced by ammonium sulphide be changed from gelatinous to granular? Give the formulæ for all compounds thrown down by ammonium sulphide from the known solution containing Groups III and IV. Why must the precipitate caused by ammonium sulphide be filtered as rapidly as possible? Why must this precipitate be washed with hot water? Why must this precipitate be dissolved in dilute, instead of in concentrated, hydrochloric acid?

What may a black residue from the hydrochloric acid treatment contain? How is the borax bead test applied? What is the color of the cobalt bead? Of the nickel bead? Which metal is likely to obscure the other in the bead test? How is aqua regia made? Write the equation for the production of nascent chlorine in aqua regia. Write the equation for the solubility of three molecules of cobalt sulphide in six molecules of hydrochloric acid and two molecules of nitric acid. Why must only the smallest possible quantity of aqua regia be used? Why must ammonium salts be expelled before testing for cobalt and nickel?

If the solution supposed to contain Fe, Mn, Zn, Al, and Cr is colorless, would you consider chromium present or absent?

What color must the solution have if chromium is present? If the solution is colorless and dilute, what simple step is advisable before deciding definitely on the presence or absence of chromium?

Why must the solution containing Fe, Mn, Zn, and Al be boiled till H_2S is all expelled? What change does boiling with nitric acid bring about in the solution? Why is this change in the iron advisable? Why must the excess of free acid be driven off by boiling? What impurity is often present in sodium hydrate solution that has stood for some time? In the place of what metal is this impurity likely to appear later? Why must an excess of sodium hydrate solution be added? What two metals may come down in small quantity along with the precipitate of ferric hydrate and manganese hydrate? Is it necessary to remove traces of these two metals before proceeding with the tests for iron and manganese? Why must the solution containing iron be diluted with water before potassium ferrocyanide is added? If iron is found present, why is it necessary to test for ferrous and ferric iron in the original solution? What compound of manganese is formed when manganese hydrate is fused with sodium carbonate? How may the platinum foil be tested to insure absolute absence of manganese in its folds?

What compound of zinc is present in the sodium hydrate solution of zinc? What corresponding aluminium compound is present in the sodium hydrate solution? Why is it necessary to pass only a little hydrogen sulphide into the solution supposed to contain zinc? What substance sometimes precipitates in the place of zinc sulphide, and how can you distinguish between this precipitate and zinc sulphide? Why must an excess of ammonium hydrate be used in testing for aluminium? In what respect does aluminium hydrate differ from many other white precipitates? What substance may appear in the place of aluminium hydrate in the regular scheme? How did this substance get into the solution? How can you distinguish between this substance and aluminium hydrate?

If Cr is present in an unknown solution, what reagent is used that is not used when Cr is absent? What three metals does the barium carbonate separate as precipitates? Give the formulæ for the compounds of Al, Fe, and Cr precipitated by barium carbonate. Why is it advisable to neutralize the free nitric acid with sodium carbonate before adding barium carbonate? Why must care be taken that the sodium carbonate does not form a precipitate? Why must the precipitate containing the excess of barium carbonate be dissolved in dilute rather than in concentrated hydrochloric acid? Why must the barium sulphate be precipitated hot? Why must the sodium hydrate solution containing Fe, Al, and Cr be boiled before filtering? How is chromium oxidized from the basic state to the acid state? What is the color of chromium chloride solution? Of sodium chromate solution? What two reagents are added to the solution containing sodium chromate to confirm the presence of chromium? Give the color, formula, and solubility in water of lead chromate.

400. Groups I to IV of Bases. — In a solution containing the first four groups of bases why add ammonium chloride? Why add ammonium hydrate? Why add ammonium sulphide? What metals are contained in the filtrate from the precipitation with ammonium sulphide? Why must the ammonia which is added at the beginning not be in large excess? Why should the filtrate containing Groups I and II be colorless? What impurity is probably present if this filtrate is black or brown, and how may this impurity be removed? What impurity is probably present if this filtrate is pink, and how may this impurity be removed? What impurity causes the filtrate containing Groups I and II to become turbid when standing in air or when warmed? How may an excess of ammonium sulphide in this filtrate be removed? Does the examination of the filtrate containing Groups I and II differ any from the analysis of a solution which originally contained only Groups I and II?

401. Group V of Bases. — Give the name and symbol of each of the six members of Group V of Bases. Which members of

this group exist in both *ous* and *ic* states? To which state of oxidation do most of the copper salts belong? Give the formula for mercurous nitrate. For mercuric chloride. For cadmium nitrate. For silver nitrate. For bismuth nitrate.

Which members of Group V give a precipitate with dilute hydrochloric acid? What is the action of ammonium hydrate on silver chloride? On lead chloride? On mercurous chloride? What is the solubility of lead chloride in cold water? In hot water? What is the solubility in nitric acid of the precipitates produced by ammonium hydrate in mercurous and in mercuric solutions? What is the solubility in nitric acid of precipitates produced by ammonium hydrate in solutions of the other members of this group? Give the color, formula, and solubility in hot dilute nitric acid of the sulphide of each member of Group V. What combination of acids must be used to dissolve mercuric sulphide? Which member of this group forms a basic precipitate when its solution is diluted with water?

Why is an unknown solution containing mercuric chloride not likely to contain silver and lead? If dilute hydrochloric acid produces no precipitate in a solution said to contain metals of Group V, what two metals are thereby shown absent without a doubt? What third metal is probably also absent? What is the formula of the white precipitate that dilute hydrochloric acid occasionally throws down if this precipitate is soluble in excess of the acid? Why must a slight excess of hydrochloric acid be added to a solution of Group V metals? Why must a large excess of the acid be avoided? Why is it wise to shake the precipitate caused by HCl?

Why must the precipitated chlorides be washed with cold water? Why must they then be brought to a boil with considerable water? Why must the residue containing silver chloride and mercurous chloride be washed with hot water? What effect does ammonium hydrate have on precipitated silver chloride? On precipitated mercurous chloride? What is the quickest test to apply to verify the presence of lead? What more reliable test might be applied? Why does lead

appear in two places in the regular analysis? What reagent removes the most of the lead? What reagent finally removes the rest of the lead?

What salts may be present in the filtrate from the precipitated chlorides? Give the formulæ of the sulphides thrown down by hydrogen sulphide. What effect does the presence of much hydrochloric acid or nitric acid have on the precipitation with hydrogen sulphide? If the solution contains much free nitric acid, what treatment is advisable before passing in hydrogen sulphide? What metal is probably present if the original solution contained much free nitric acid? How may the presence of this metal be determined easily in the original solution? How may complete precipitation by hydrogen sulphide be shown? What is the general color of the precipitate caused by hydrogen sulphide? If hydrogen sulphide produced a yellow precipitate, what metal was probably present? If hydrogen sulphide produced a precipitate that was white at first, but changed through yellow and red to black, what metal was probably present?

What is the effect upon mercuric sulphide of boiling with dilute nitric acid? What is the effect on the sulphides of Pb, Cu, Cd, and Bi of boiling with dilute nitric acid? Why does not a black residue after boiling with nitric acid indicate conclusively the presence of mercury? What is the confirmatory test for mercuric mercury?

With what reagent is the last portion of lead removed? Why is it necessary to boil till white fumes of sulphuric acid appear? Why is it necessary to dilute with water before filtering off the lead sulphate? What metal may occasionally appear in the white precipitate produced by ammonium hydrate in the solution containing Cu, Cd, and Bi? What is the confirmatory test for bismuth? If the filtrate from bismuth hydrate is blue, what metal is present? If the filtrate is not blue, how may the presence of a trace of copper be shown? If copper is absent, is treatment with potassium cyanide solution necessary before testing for cadmium?

402. Groups I to V of Bases. — In a solution containing the first five groups of bases why add hydrochloric acid? What metals are contained in the filtrate from the precipitated chlorides? What metals are separated from the solution by treatment with hydrogen sulphide? What metals are contained in the filtrate from the precipitated sulphides of Group V? What metals are precipitated by treatment with ammonium chloride, ammonium hydrate, and ammonium sulphide? What metals are contained in the filtrate from the precipitate containing Groups III and IV?

Why must cold dilute hydrochloric acid be used in precipitating Ag, Pb, and Hg? Why should not hydrogen sulphide be passed into a strongly acid solution? Why must the precipitated sulphides be washed free from the solution containing the metals of Groups III and IV? Is complete precipitation probable if the solution into which hydrogen sulphide is passed is boiling? Why? Which members of Group V are likely to run into the filtrate containing Groups I to IV? How may their presence there be shown? How may the traces of these metals be removed before treatment with ammonium sulphide? Why is the addition of ammonium hydrate to the filtrate containing Groups I to IV often likely to produce a black precipitate? Does the formation of this black precipitate show that any mistake has been made in the early work on the solution?

403. Group VI of Bases. — Give the name and symbol of each of the three members of Group VI of Bases. Which members occur in both states of oxidation? Which state of arsenic did we study? Which of antimony? What is the formula for arsenous chloride? For antimonous chloride? For stannous chloride? For stannic chloride? Which member of Group VI gives a basic precipitate when its solution is diluted with water? What is the formula for this basic precipitate?

What precipitates are caused by hydrochloric acid in solutions of the members of Group VI? Give the color and formula for the precipitate produced by hydrogen sulphide in

an arsenic solution. In an antimony solution. In a stannous solution. In a stannic solution. What is the solubility of the sulphides of Group VI in dilute hydrochloric acid? In concentrated hydrochloric acid? In concentrated ammonium carbonate solution? In yellow ammonium sulphide? Give the formulæ of the compounds thrown out by hydrochloric acid from the solutions of the sulphides of Group VI in yellow ammonium sulphide.

What acid is likely to be present in a solution containing the metals of Group VI? What compound may be thrown out from a Group VI solution when it is diluted with water? Why is it not necessary to put this white precipitate into solution again before passing in hydrogen sulphide? What is meant by the colloidal state? How may precipitation of Group VI metals be made complete if the colloidal state manifests itself? Which member of Group VI is precipitated slowly by hydrogen sulphide?

How may As be separated from Sb and Sn? Why is the residue containing As_2S_3 likely to contain traces of Sb and Sn? Why is the solution containing Sb and Sn likely to contain traces of As? How may the dissolving of the As_2S_3 during treatment with HCl be prevented? What reagent is used to put the As_2S_3 residue into solution? How can you tell when the chlorine has all been boiled off? Why must it be boiled off? What reagent removes the traces of Sb and Sn from the solution containing As? What compound have you had that was similar to the magnesium ammonium arsenate precipitate? What compound of As is present in the solution containing Sb and Sn if traces of As are also present? Describe the safety tube test for lighting hydrogen. What effect does nascent hydrogen have on the tin in the solution? What metal deposits on the zinc in the generator? What is the color of the Sb deposit on the platinum foil? How may an Sb mirror be distinguished from an As mirror?

The presence of tin was shown by precipitating mercurous chloride by means of a solution of mercuric chloride. What is

there about this test that differentiates it from all other tests by precipitation that you have tried?

404. Groups I to VI of Bases. — What part of the scheme for separating all the metals into groups is common to work already done? In a solution containing all six groups why add hydrochloric acid? What metals are precipitated by the treatment with hydrogen sulphide? How may the Group VI metals be separated from the rest of the Group V metals? What compound of antimony may be produced by dilute hydrochloric acid in the original solution? What metals of Groups V and VI may be present in small quantity in the filtrate containing Groups I to IV? How may these traces be removed? Why must the precipitated sulphides of Groups V and VI be washed with hot water till the wash water is no longer acid? Why must a large excess of yellow ammonium sulphide be avoided?

405. Acids. — Give the names and formulæ of the acids of Group I. Of the acids of Group II. Of the acids of Group III. What name is sometimes given to Group I of acids? To Group II of acids? Which of these acids are organic acids? What is the prevailing color of the precipitates produced by barium chloride in solutions of Group I acids? What is the prevailing solubility of the barium salts of Group I acids in hydrochloric acid? In acetic acid? Which barium salt is insoluble in all acids? What is the prevailing color of the precipitates produced by calcium chloride in solutions of Group I acids? What is the prevailing color of the precipitates produced by silver nitrate in solutions of Group I acids? What is the solubility in nitric acid of the silver salts of Group I acids? What is the solubility in water of the barium salts of Group II acids? Of the corresponding calcium salts? Give the color, formula, and solubility in nitric acid, in ammonium hydrate, and in potassium cyanide of silver chloride. Of silver bromide. Of silver iodide. Of silver cyanide. Of silver ferrocyanide. Of silver ferricyanide. Of silver sulphide.

What is the special test for sulphurous acid? For thiosul-

phuric acid? For phosphoric acid in solutions of phosphates that are soluble in water? What is the special test for sulphuric acid? For carbonic acid? For hydrochloric acid? For hydrobromic acid? For hydriodic acid? For nitric acid? For chloric acid? For acetic acid?

How may arsenic and chromium be removed before testing with barium chloride for Group I acids? How may sulphurous acid, thiosulphuric acid, and carbonic acid be removed before testing with barium chloride? When is it advisable to use the test with calcium chloride? When is it unnecessary? How may hydrogen sulphide be removed before testing for Group II acids? Why is it necessary to add nitric acid before adding silver nitrate in the test for Group II acids.

406. Salts. — Which part of a salt should be determined first, the base or the acid radical? What is meant by the preliminary analysis of a salt? Why is it advisable to try this preliminary analysis? What seven items are included in the preliminary analysis?

What three kinds of water may be shown present by the bulb tube test? What does a black residue in the bulb tube indicate? What does a white sublimate in the bulb tube indicate? What is the best method for heating on charcoal? What does deflagrating on charcoal indicate? Which metals give malleable globules on fusion with sodium carbonate on charcoal? Which metal gives a good coating on charcoal? What metal gives a blue borax bead? What metal gives a green borax bead in the inner flame? What metal gives a reddish brown bead in the outer flame? Mention nine metals whose presence may be shown by the flame test. What acid radicals may be shown present by treatment with concentrated sulphuric acid?

What is the best way to dissolve a salt in water? How may the solubility in water of a substance sparingly soluble or apparently insoluble be tested? What is the best acid in which to dissolve substances insoluble in water? What is the next best acid? What combination of acids is used as a final re-

sort? What is the best acid to use in dissolving a metal? What two metals are oxidized to the oxides by treatment with nitric acid? Why is it advisable to add water after treating an insoluble substance with an acid?

If an unknown salt is soluble in water and only alkali metals are present, what acids may be present? If a salt is soluble in water and only barium is present, what acids must be absent and what acids may be present? If a salt is soluble in water and only lead is present, what acid tests may be omitted?

What are the more common substances that are insoluble in water and acids? To what treatment is an insoluble substance generally subjected? What insoluble substances may be decomposed by boiling with sodium hydrate solution? What substances must be removed before an insoluble substance is fused? How may free sulphur be removed? How may free carbon be removed? How may lead sulphate be removed? How may the halogen salts of silver be removed?

Why must not silver and lead be fused in a platinum crucible? What is the ordinary mixture used in the fusion of an insoluble substance? What third substance is sometimes added? What reaction takes place during the fusion with sodium carbonate? What substances are unaffected by fusion with sodium carbonate? What insoluble substance is decomposed by hydrofluoric acid? What three metallic oxides are most easily fused with acid potassium sulphate?

If an unknown substance is partly soluble in water, partly soluble in acids, and partly insoluble in both water and acids, which portion should be examined first? Why?

COMPLETE LIST OF REAGENTS NEEDED FOR THE WORK INDICATED IN THIS BOOK

407. The general use of *commercial* chemicals as reagents should be avoided as far as possible. Students generally look for sharp and conclusive reactions, and every instructor in

Qualitative Analysis knows how hard it is to get such results every time, even with the best of reagents. Why, therefore, run the risk of confusing the student by giving him reagents that often are likely to switch his attention off from the main work? It is the opinion of the author that in analytical work for the first year it is economy in the end to use only the purest reagents obtainable. Enough of commercial chemicals are on hand in every laboratory to give the student practice later in the course with "traces" and "secondary reactions" if such work is desired.

Individual Reagents

408. As stated in section 7, each student, when he begins his laboratory work, should be supplied with a set of individual liquid reagents kept in 500 c.c. glass-stoppered bottles with blown labels. The following list indicates the proper strength of each of these solutions and the method of preparing those solutions that cannot be made by simply dissolving the substance in water:

Acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$. One part of glacial acetic acid to two and a half parts of water.

Hydrochloric acid, concentrated, HCl . Full strength of chemically pure acid.

Hydrochloric acid, dilute, HCl . One volume of concentrated acid to five volumes of water.

Nitric acid, concentrated, HNO_3 . Full strength of chemically pure acid.

Nitric acid, dilute, HNO_3 . One volume of concentrated acid to five volumes of water.

Sulphuric acid, concentrated, H_2SO_4 . Full strength of chemically pure acid.

Sulphuric acid, dilute, H_2SO_4 . Add *slowly* one volume of concentrated acid to five volumes of water and shake the mixture thoroughly.

Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$. Mix one part of sesquicarbonate of ammonium (the "ammonium carbonate" of trade),

four parts of water, and one part of concentrated ammonium hydrate. Do not heat the mixture, but allow it to digest in a closed bottle till all the salt is dissolved.

Ammonium chloride, NH_4Cl . Dissolve one part of the salt in ten parts of water.

Ammonium hydrate, NH_4OH . Dilute one part of concentrated aqua ammonia with four parts of water.

Ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Dissolve one part of the crystallized salt in twenty-five parts of water.

Ammonium sulphide, colorless, $(\text{NH}_4)_2\text{S}$. Dilute 250 c.c. of concentrated aqua ammonia with 250 c.c. of water in a 500 c.c. reagent bottle. Into 400 c.c. of the resulting liquid pass H_2S till the liquid has lost its strong ammoniacal odor and has taken on a strong odor of sulphide of hydrogen. The proper point has been reached when a few c.c. of the liquid will no longer give a precipitate with MgSO_4 when heated a little. Then discontinue passing in H_2S and add the other 100 c.c. of dilute ammonia. This solution deteriorates easily on standing, and a fresh solution should be made up occasionally.

Ammonium sulphide, yellow, $(\text{NH}_4)_2\text{S}_2$. Allow the colorless ammonium sulphide to stand for a few weeks, or add a very little flowers of sulphur to some of the colorless ammonium sulphide and allow to stand an hour.

Barium chloride, BaCl_2 . 1:10.

Calcium chloride, CaCl_2 . 1:10.

Calcium sulphate, CaSO_4 . Powder some crystallized gypsum and digest an excess of it with water for some time; let the undissolved part settle and then decant the saturated solution.

Lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. 1:10.

Silver nitrate, AgNO_3 . 1:40.

Sodium hydrate, NaOH . 1:10. When the sodium hydrate has dissolved, allow the solution to settle and then decant from any sediment that may have formed. This solution, of course, cannot be filtered through filter paper.

Sodium phosphate, Na_2HPO_4 . 1:10.

General Reagents

409. In addition to the individual reagents described above, a few sets of the following reagents should be put out for the general use of the class. The number of sets will depend, of course, on the size of the class. In all cases they should be within easy reach of the student.

Alcohol. Use commercial ethyl alcohol.

Ammonium acetate, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. Dissolve the crystallized salt in water, or neutralize some aqua ammonia with acetic acid.

Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3 + \text{Aq.}$ Make a saturated solution by dissolving an excess of the salt in water without the aid of heat.

Ammonium chloride, NH_4Cl . Crystallized salt.

Ammonium molybdate, $(\text{NH}_4)_2\text{MoO}_4 + \text{Aq.}$ Dissolve 60 grams of the dry salt in 400 c.c. of aqua ammonia; add 400 c.c. of water; then add slowly 500 c.c. of concentrated nitric acid.

Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4 + \text{Aq.}$ 1:10.

Barium carbonate emulsion, $\text{BaCO}_3 + \text{Aq.}$ Grind precipitated BaCO_3 with water till the emulsion is free from lumps.

Barium hydrate, BaO_2H_2 . Saturated solution and solid.

Calcium fluoride, CaF_2 . Powder.

Calcium hydrate, CaO_2H_2 . Dry, amorphous, air-slaked lime.

Carbon bisulphide, CS_2 .

Chlorine water, $\text{Cl}_2 + \text{Aq.}$ Make up fresh occasionally.

Ether-alcohol mixture, $(\text{C}_2\text{H}_5)_2\text{O} + \text{C}_2\text{H}_5\text{OH}$. Equal portions by volume of ether and of absolute alcohol.

Hydrofluoric acid. Use commercial acid.

Hydrogen sulphide, H_2S . This gas should be supplied to the class from a generator capable of delivering under constant pressure. The generator devised by Professor C. L. Parsons of New Hampshire Agricultural College is probably the best one.

Iron filings, Fe. Use filings free from oil.

Iron wire, Fe. Use small wire staples.

Iron chloride, ferric chloride, $\text{FeCl}_3 + \text{Aq.}$ 1:10.

Iron sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Crystals.

Iron sulphide, FeS. Lumps.

- Lead nitrate*, $\text{Pb}(\text{NO}_3)_2$. Crystalline lumps.
- Lithium chloride*, LiCl . Crystals.
- Litmus paper*, blue.
- Magnesium chloride*, $\text{MgCl}_2 + \text{Aq.}$ 1 : 4.
- Magnesium sulphate*, $\text{MgSO}_4 + \text{Aq.}$ 1 : 10.
- Manganese dioxide*, MnO_2 . Powder.
- Mercuric chloride*, $\text{HgCl}_2 + \text{Aq.}$ 1 : 10.
- Platinum chloride*, $\text{H}_2\text{PtCl}_6 + \text{Aq.}$ Dilute some concentrated platinum chloride solution of trade with several volumes of water.
- Potassium acetate*, $\text{KC}_2\text{H}_3\text{O}_2 + \text{Aq.}$ 1 : 10.
- Potassium bromide*, KBr . Crystals.
- Potassium carbonate*, K_2CO_3 . Dry powder.
- Potassium chlorate*, KClO_3 . Crystals.
- Potassium chromate*, $\text{K}_2\text{CrO}_4 + \text{Aq.}$ 1 : 10.
- Potassium cyanide*, KCN . Fused lumps.
- Potassium ferrocyanide*, $\text{K}_4\text{Fe}(\text{CN})_6 + \text{Aq.}$ 1 : 15.
- Potassium ferricyanide*, $\text{K}_3\text{Fe}(\text{CN})_6$. The solution does not keep. Use the crystals or powder.
- Potassium iodide*, KI . Crystals.
- Potassium nitrite*, $\text{KNO}_2 + \text{Aq.}$ 1 : 2.
- Potassium sulphate, acid*, KHSO_4 . Crystals or powder.
- Potassium sulphocyanide*, $\text{KSCN} + \text{Aq.}$ 1 : 15.
- Sand*, SiO_2 . Use clean sea sand.
- Sodium acetate*, $\text{NaC}_2\text{H}_3\text{O}_2$. Crystals and concentrated solution.
- Sodium borate*, $\text{Na}_2\text{B}_4\text{O}_7$. Powdered borax.
- Sodium carbonate*, Na_2CO_3 . Use both the dry powdered, anhydrous salt and a concentrated solution.
- Sodium hypochlorite*. Crystals.
- Sodium peroxide*, Na_2O_2 . Dry powder. Keep well stoppered.
- Sodium potassium tartrate*, $\text{NaKC}_4\text{H}_4\text{O}_6$. Crystals.
- Sodium sulphite*, Na_2SO_3 . Dry salt.
- Sodium thiosulphate*, $\text{Na}_2\text{S}_2\text{O}_3$. Dry salt.
- Strontium chloride*, $\text{SrCl}_2 + \text{Aq.}$ 1 : 10.
- Tin chloride*, $\text{SnCl}_2 + \text{Aq.}$ Stannous chloride. 1 : 10. For preparation see section 417.
- Turmeric paper*.

410. Reagents to be used in Preliminary Work for Bases and for Making up Unknown Solutions

FOR PRELIMINARY WORK	FOR UNKNOWN SOLUTIONS
Na_2CO_3 . . . Use general reagent.	$\text{NaNO}_3 + \text{Aq}$ 1:10.
KClO_3 . . . Use general reagent.	$\text{KNO}_3 + \text{Aq}$ 1:10.
LiCl Use general reagent.	$\text{LiNO}_3 + \text{Aq}$ 1:10.
NH_4Cl . . . Use general reagent.	$\text{NH}_4\text{NO}_3 + \text{Aq}$ 1:10.
$\text{BaCl}_2 + \text{Aq}$. 1:10. Use individual reagent.	$\text{Ba}(\text{NO}_3)_2 + \text{Aq}$ 1:10.
$\text{SrCl}_2 + \text{Aq}$. 1:10. Use general reagent.	$\text{Sr}(\text{NO}_3)_2 + \text{Aq}$ 1:10.
$\text{CaCl}_2 + \text{Aq}$. 1:10. Use individual reagent.	$\text{Ca}(\text{NO}_3)_2 + \text{Aq}$ 1:10.
$\text{MgSO}_4 + \text{Aq}$. 1:10. Use general reagent.	$\text{Mg}(\text{NO}_3)_2 + \text{Aq}$ 1:10.
$\text{Al}(\text{NO}_3)_3 + \text{Aq}$ 1:40.	$\text{Al}(\text{NO}_3)_3 + \text{Aq}$ 1:10.
$\text{Cr}(\text{NO}_3)_3 + \text{Aq}$ 1:40.	$\text{Cr}(\text{NO}_3)_3 + \text{Aq}$ 1:10.
$\text{FeSO}_4 + \text{Aq}$. . . See section 34.	$\text{FeSO}_4 + \text{Aq}$. . . See section 34.
$\text{Fe}(\text{NO}_3)_3 + \text{Aq}$ 1:40.	$\text{Fe}(\text{NO}_3)_3 + \text{Aq}$ 1:10.
$\text{Co}(\text{NO}_3)_2 + \text{Aq}$ 1:40.	$\text{Co}(\text{NO}_3)_2 + \text{Aq}$ 1:10.
$\text{Ni}(\text{NO}_3)_2 + \text{Aq}$ 1:10.	$\text{Ni}(\text{NO}_3)_2 + \text{Aq}$ 1:10.
$\text{Mn}(\text{NO}_3)_2 + \text{Aq}$ 1:40.	$\text{Mn}(\text{NO}_3)_2 + \text{Aq}$ 1:10.
$\text{Zn}(\text{NO}_3)_2 + \text{Aq}$ 1:40.	$\text{Zn}(\text{NO}_3)_2 + \text{Aq}$ 1:10.
$\text{AgNO}_3 + \text{Aq}$. 1:40. Use individual reagent.	$\text{AgNO}_3 + \text{Aq}$ 1:40.
$\text{Pb}(\text{NO}_3)_2 + \text{Aq}$ 1:40.	$\text{Pb}(\text{NO}_3)_2 + \text{Aq}$ 1:10.
$\text{HgNO}_3 + \text{Aq}$. . . See section 411.	$\text{HgNO}_3 + \text{Aq}$. . . See section 411.
$\text{HgCl}_2 + \text{Aq}$ 1:40.	$\text{HgCl}_2 + \text{Aq}$. . . Saturated solution.
$\text{Cu}(\text{NO}_3)_2 + \text{Aq}$ 1:40.	$\text{Cu}(\text{NO}_3)_2 + \text{Aq}$ 1:10.
$\text{Cd}(\text{NO}_3)_2 + \text{Aq}$ 1:40.	$\text{Cd}(\text{NO}_3)_2 + \text{Aq}$ 1:10.
$\text{Bi}(\text{NO}_3)_3 + \text{Aq}$. . . See section 412.	$\text{Bi}(\text{NO}_3)_3 + \text{Aq}$. . . See section 412.
$\text{AsCl}_3 + \text{Aq}$. 1:40. See section 414.	$\text{AsCl}_3 + \text{Aq}$. 1:10. See section 413.
$\text{SbCl}_3 + \text{Aq}$. 1:40. See section 416.	$\text{SbCl}_3 + \text{Aq}$. 1:10. See section 415.
$\text{SnCl}_2 + \text{Aq}$. 1:40. See section 418.	$\text{SnCl}_2 + \text{Aq}$. 1:10. See section 417.
$\text{SnCl}_4 + \text{Aq}$. 1:40. See section 420.	$\text{SnCl}_4 + \text{Aq}$. 1:10. See section 419.

411. *Mercurous nitrate*, $\text{HgNO}_3 + \text{Aq.}$ Make a saturated solution of mercurous nitrate and add a few drops of mercury to keep the salt in the mercurous state.

412. *Bismuth nitrate*, $\text{Bi}(\text{NO}_3)_3 + \text{Aq.}$ Treat an excess of powdered bismuth subnitrate with concentrated nitric acid. Dilute some of the clear solution with water; if a white precipitate forms, add just enough nitric acid to dissolve it.

413. *Arsenic chloride*, $\text{AsCl}_3 + \text{Aq.}$ 1:10. Boil 50 grams As_2O_3 with enough concentrated HCl to dissolve it. Let cool to ordinary temperature. If any white precipitate separates, discard this and take the clear solution, which should be about 50 c.c.; add 450 c.c. of water and boil till it is clear.

414. *Arsenic chloride*, $\text{AsCl}_3 + \text{Aq.}$ 1:40. To 100 c.c. of $\text{AsCl}_3 + \text{Aq.}$ 1:10 solution, add 300 c.c. of water; boil till clear.

415. *Antimony chloride*, $\text{SbCl}_3 + \text{Aq.}$ 1:10. Mix 50 c.c. of chemically pure antimony chloride solution of trade, 75 c.c. of concentrated HCl , and 375 c.c. of water. The solution should be clear. If it is milky on account of separation of SbOCl , add a little more HCl .

416. *Antimony chloride*, $\text{SbCl}_3 + \text{Aq.}$ 1:40. To 100 c.c. of $\text{SbCl}_3 + \text{Aq.}$ 1:10 solution, add 50 c.c. of concentrated HCl and 250 c.c. of water. The solution should be clear; if it is not, add a little more HCl .

417. *Tin chloride, stannous chloride*, $\text{SnCl}_2 + \text{Aq.}$ 1:10. Dissolve 50 grams of stannic chloride, SnCl_4 , in 500 c.c. of water, add a little mossy Sn and heat for about 10 minutes to reduce the stannic chloride to stannous chloride. Keep in a bottle containing mossy tin.

418. *Tin chloride, stannous chloride*, $\text{SnCl}_2 + \text{Aq.}$ 1:40. To 100 c.c. of $\text{SnCl}_2 + \text{Aq.}$ 1:10 solution, add 300 c.c. of water.

419. *Tin chloride, stannic chloride*, $\text{SnCl}_4 + \text{Aq.}$ 1:10. Dissolve 50 grams of stannic chloride, SnCl_4 , in 500 c.c. of water by means of heat. The solution should be clear and should give no precipitate with $\text{HgCl}_2 + \text{Aq.}$

420. *Tin chloride, stannic chloride*, $\text{SnCl}_4 + \text{Aq.}$ 1:40. To 100 c.c. of $\text{SnCl}_4 + \text{Aq.}$ 1:10 solution, add 300 c.c. of water.

421. Reagents to be used in Preliminary Work for Acids

$K_2CrO_4 + Aq$. . .	1:40.	$Na_2SO_4 + Aq$. . .	1:40.
$Na_3AsO_3 + Aq$. . .	1:40.	$NaCl + Aq$	1:40.
$Na_3AsO_4 + Aq$. . .	1:40.	$KBr + Aq$	1:40.
$Na_2SO_3 + Aq$. . .	1:40.	$NaI + Aq$	1:40.
$Na_2S_2O_3 + Aq$. . .	Conc.	$KCN + Aq$	1:40.
$Na_2HPO_4 + Aq$. . .	1:40.	$K_4Fe(CN)_6 + Aq$. . .	1:40.
$Na_2B_4O_7 + Aq$. . .	1:40.	$K_6Fe_2(CN)_{12} + Aq$. . .	1:40.
$(NH_4)_2C_2O_4 + Aq$. . .	1:40.	$(NH_4)_2S + Aq$. . .	Individual reagent.
$NaF + Aq$	1:40.		
$NaKC_4H_4O_6 + Aq$. . .	1:20.	$KNO_3 + Aq$	1:40.
$Na_2CO_3 + Aq$	1:40.	$KClO_3 + Aq$	1:40.
$Na_2SiO_3 + Aq$. . .	1:40.	$NaC_2H_3O_2 + Aq$. . .	1:40.

SUGGESTIONS TO THE TEACHER

422. The preface to this book sets forth the motif of the author and indicates how the text is used in his classes. Many suggestions, therefore, that would naturally be looked for here will be found fully set forth in the preface. The following suggestions are inserted, however, to emphasize certain points already touched upon, and to include hints which may be of help in using this text, but which are not given elsewhere.

The author has found it of distinct advantage to his pupils to try at the lecture desk all the tests in the Preliminary Work tables, and then to require each student to repeat this work for himself; this enables the instructor to make doubly sure that all the solutions are in condition to give the reactions noted in the text, and to make any additional remarks he feels the class needs. For the same reasons it is desirable to analyze on the lecture desk before the class known solutions containing all the members of each group of bases.

Much care has been devoted to details in developing the

schemes for analysis. When definite amounts of reagents are specified, it is understood that all reagents and solutions are made up according to the directions given in the Appendix. This point must be kept constantly in mind, for every teacher of chemical analysis knows — perhaps to his sorrow — to what extent slight changes in the conditions may affect the success of an experiment.

It is impossible to say definitely how much time is necessary to complete the work laid out in these pages, for this depends so much upon the number of bases given in the unknown solutions and upon the character of the salts given out for analysis. The text divides itself conveniently for twenty-seven weeks' work, though this may be reduced in case of necessity by the omission of work on the combinations of groups of bases. Such omissions, however, are not advised. In no case should any preliminary work be omitted, for this is the foundation on which the analytical structure stands. The author tries to plan the unknown solutions and salts so that each student shall not spend less than six nor more than ten hours per week in laboratory work.

The instructor should always be within easy reach of the pupil for appeal in case of difficulty with text or solutions, but the pupil should be encouraged to solve his own difficulties as far as possible. The frequent use of blank tests on the stock solutions will generally enable the student to solve his difficulties himself.

Lack of clearness in the student's mind as to the proper method to pursue is often due to lack of familiarity on his part with the facts learned in the Preliminary Work; hence the need of referring him constantly to this work.

The notebook should contain a record of all work done in the laboratory and this record be made *in ink and at the time the experiment is done*. This record should be examined carefully by the instructor in the presence of the pupil as soon as convenient after the solution or salt has been finished. The instructor's comments and corrections should be made in red

ink. The student should save the unknown solution or salt till after the report has been made, in case he has to repeat the analysis or in case the instructor wishes to verify any test.

Too much stress should not be laid upon the preliminary analysis of salts, because the correct interpretation of reactions occurring therein requires long practice. Furthermore, many of the reactions in this preliminary examination do not by their absence indicate the absence of certain bases or acid radicals.

For the use of those students who do not find this text full enough, Treadwell's *Qualitative Analysis* will be found admirably suited for reference.

The complete analysis of an unknown must show not only what substances are present, but also that all other substances are absent.

A collection of the chemical elements and compounds as they occur in nature and as they are found in the laboratory is a distinct help to the students if exhibited in such place and form as to be accessible to the members of the class. The author uses a collection of about fifteen hundred such specimens to good advantage.

It goes without saying that students of Qualitative Analysis should work independently, and should be unprejudiced by what their neighbors find in their unknown solutions and salts. They should be taught, if a test is unsatisfactory, first to find the probable cause of error, and then to repeat the work. Furthermore, orderliness, cleanliness, use of common sense, and willingness and ability to follow instructions faithfully and understandingly are essential to success in analytical work.

It is also of the greatest importance that the student should agree with himself to see results *exactly* as they present themselves, and refuse to allow himself to be prejudiced in his observation by what he may think is present or by what he may hope to find present. This attitude of absolute honesty is more easily attained by the student if he comes in contact with it in all tests that the instructor may find it necessary to make in connection with the student's work.

INDEX

(References are to sections.)

A

Abbreviations, 13.
Acetic acid, reactions, 296.
 acid, test, 326.
Acid analysis, 288 to 330.
 analysis of salts limited by bases present, 365 to 370.
 analysis, scheme, 327 to 330.
 potassium sulphate, used as a flux, 387.
Acids, 12.
 Group I, list, 289.
 Group I, scheme, 328.
 Group II, list, 290.
 Group II, scheme, 329.
 Group III, list, 291.
 Group III, scheme, 330.
 list, 288.
 organic, 288.
 special tests, 301.
 table of preliminary work, 296.
Action of salts with sulphuric acid, 340.
Alcohol, 282.
Alkali Group, list, 15.
 metals in natural silicates, special tests, 385.
Alkaline-earth Group, list, 16.
 metals sometimes found in Groups III and IV, 272 to 277.
Alloys, action with acids, 359 to 361.
Aluminium Group, list, 17.
 hydrate, how distinguished from silica, 133.
 hydrate, precipitated by ammonium sulphide, 82.
 hydrate, properties, 82.
 reactions, 82.
 test unsatisfactory, 134.
Ammonium chloride, effect on Group II, 49.
 chloride, effect on Groups III and IV, 82, 104.

hydrate, effect on Group II, 50.
 hydrate, effect on Groups I to IV, 168.
 hydrate, effect on Groups III and IV, 105, 106.
 hydrate, precipitates caused by, 82, 106, 172, 200.
 test, 26.
Analysis, Acid, 288 to 330.
 Basic, 14 to 287.
 of natural silicates, 385.
 Qualitative, definition, 1.
 Salt, 331 to 390.
Antimonous sulphide, properties, 229.
Antimony, mirror, 253.
 oxychloride, 229, 240, 262.
 reactions, 229.
 sulphide, colloidal, 241.
 sulphide, properties, 229.
 trace in filtrate from Groups V and VI, 265.
Apparatus, list, 10.
Aqua regia, composition, 362.
 treatment of salts with, 362.
Arsenic acid, reactions, 296.
 acid, test, 305.
 mirror, 253.
 reactions, 229.
 sulphide, colloidal, 241.
 sulphide, precipitated slowly from an arsenate, 242.
 sulphide, properties, 229.
Arsenous acid, reactions, 296.
 acid, test, 304.
 sulphide, properties, 229.

B

Barium carbonate emulsion, 136.
 carbonate, properties, 38.
 chloride group of acids, 289.
 chromate, properties, 38.
 flame test, 38.
 hydrate, use as a flux, 385.

(References are to sections.)

- Barium** oxalate, properties, 38.
 phosphate, properties, 38.
 reactions, 38.
 removal, in Group II, 58.
 removal, in Groups III and IV, 102.
 sulphate, properties, 38.
- Bases**, 12.
 complete list, 14.
 Group I, list, 15, 24.
 Group II, list, 16, 35.
 Group III, list, 17, 80.
 Group IV, list, 18, 80.
 Group V, list, 19, 170.
 Group VI, list, 20, 227.
 removal by hydrogen sulphide, 370.
 removal by sodium carbonate, 368, 369.
- Basic Analysis**, 14 to 287.
 bismuth nitrate, properties, 172.
 oxides, decomposed by acid potassium sulphate, 387.
- Bead test**, borax, 338.
- Berthollet's Laws**, 6.
- Bismuth**, confirmatory test, 201.
 hydrate, properties, 172.
 nitrate, basic, properties, 172.
 oxychloride, 221, 262.
 oxychloride, properties, 172.
 reactions, 172.
- Bismuth sulphide**, properties, 172.
- Black** coloration, caused by ammonium hydrate, 225.
- Blank test**, 32, 327.
- Blue glass**, 25.
- Boiling** insolubles with sodium hydrate, 376.
- Borax** bead test, 338.
- Boric acid**, reactions, 296.
 acid, test, 309.
- Boyle**, 2.
- Bulb tube**, heating in, 335.
- Bumping**, how to prevent, 121.
- C**
- Cadmium** hydrate, properties, 172.
 reactions, 172.
 sulphide, orange, 194.
 sulphide, properties, 172.
 trace in filtrate from Group V, 224.
 trace in filtrate from Groups V and VI, 265.
- Calcium** carbonate, properties, 38.
 flame test, 38.
 oxalate, properties, 38.
 phosphate, properties, 38.
 reactions, 38.
 sulphate, insolubility in alcohol, 282.
 sulphate, properties, 38.
- Carbon**, removal, 378.
- Carbonic acid**, reactions, 296.
 acid, test, 313.
- Care** of reagent bottles, 8.
- Caution**, 37, 81.
- Charcoal**, heating on, 336, 337.
- Chloric acid**, reactions, 296.
 acid, test, 325.
- Chlorine**, nascent, 117, 197, 244, 246.
- Chromic acid**, reactions, 296.
 acid, test, 303.
- Chromium hydrate**, precipitated by ammonium sulphide, 82.
 hydrate, precipitated by barium carbonate, 82.
 hydrate, properties, 82.
 procedure when absent, 120.
 procedure when present, 120.
 reactions, 82.
- Coating** on charcoal, 337, 343.
- Cobalt glass**, 25.
- Cobalt**, properties, 82.
 reactions, 82, 100, 115, 117, 119.
 sulphide, properties, 82.
- Collateral reading**, 391.
- Colloidal antimony sulphide**, 241.
 arsenic sulphide, 241.
 state, 241.
 tin sulphide, 241.
- Commercial chemicals**, use, 407.
- Complete analysis** of a salt, 332.
 list of bases, 14.
 list of reagents, 407.
 precipitation, Group II, 52.
 precipitation, Groups III and IV, 108.
 precipitation, Group V, 193.
- Conditions**, knowledge of, 3, 4, 37.
- Confirmatory test** for bismuth, 201.
 test for mercury, 195.
- Contamination** of reagents, 8.
- Copper**, exists in two states, 170.
 Group, list, 19.
 hydrate, properties, 172.
 reactions, 172.
 sulphide, properties, 172.
- Copper**, test for trace, 203.
- Course** of study, 12.

(References are to sections.)

Cupric salts, 170.
Cuprous salts, 170.
Cuts, short, 140.

D

Decantate, definition, 5.
Decantation, definition, 5.
Decomposition
 of insolubles by acid potassium sulphate, 387.
 of insolubles by sodium carbonate, 383.
Dissolving precipitate on the filter paper, 53.
Division of work in Qualitative Analysis, 392.
Dry way, reaction in the, 5.

E

Emulsion, barium carbonate, 136.
Equations for Group I, scheme, 26.
 for Group II, preliminary work, 39 to 45.
 for Group II, scheme, 63 to 70.
 for Groups III and IV, preliminary work, 90 to 98.
 for Groups III and IV, scheme, 141 to 164.
 for Group V, preliminary work, 173 to 177.
 for Group V, scheme, 205 to 217.
 for Group VI, preliminary work, 230 to 236.
 for Group VI, scheme, 254 to 258.
 for phosphates and oxalates in scheme for Groups III and IV, 287.
 for preliminary work for acids, 297 to 300.
 oxidation of ferrous iron to ferric, 85.
 reduction of ferric iron to ferrous, 84.
Ether-alcohol, 56, 409.
Excess of acid, how to determine, 183.

F

Ferric chloride, reagent, 283.
 hydrate, precipitated by barium carbonate, 82.
 hydrate, properties, 82.
 iron, 83.
 iron, reduction to ferrous, 84.
Ferricyanides, decomposed by sodium hydrate, 376.

Ferrocyanides, decomposed by sodium hydrate, 376.
Ferrous hydrate, properties, 82.
 iron, 83.
 iron, oxidation to ferric, 85.
 sulphate solution, preparation, 84.
 sulphide, properties, 82.
Filtrate, definition, 5.
Filtration, definition, 5.
Flame coloration, 339.
 tests, Group I, 25.
 tests, Group II, 38.
 tests, how made, 25.
Fluxes, 382, 385, 387.
Foil, platinum, 129.
Fusion of insolubles with acid potassium sulphate, 387.
 of insolubles with sodium carbonate, 381, 382.

G

General properties of salts, 334.
 reagent, definition, 5.
 reagents, 409.
Glass, cobalt, 25.
Group I of acids, list, 289.
 I of acids, scheme, 328.
 I of bases, distinguishing characteristics, 15.
 I of bases, list, 15, 24.
 I of bases, scheme, 27.
 II of acids, list, 290.
 II of acids, scheme, 329.
 II of bases, distinguishing characteristics, 16.
 II of bases, list, 16, 35.
 II of bases, scheme, 47.
 II of bases, table of preliminary work, 38.
 III of acids, list, 291.
 III of acids, scheme, 330.
 III of bases, distinguishing characteristics, 17.
 III of bases, list, 17, 80.
 IV of bases, distinguishing characteristics, 18.
 IV of bases, list, 18, 80.
 V of bases, distinguishing characteristics, 19.
 V of bases, list, 19, 170.
 V of bases, scheme, 179.
 V of bases, table of preliminary work, 172.
 VI of bases, distinguishing characteristics, 20.

(References are to sections.)

- Group VI** of bases, list, 20, 227.
 VI of bases, scheme, 238.
 VI of bases, table of preliminary work, 229.
 alkali, list, 15.
 alkaline-earth, list, 16.
 aluminium, list, 17.
 copper, list, 19.
 iron, list, 18.
 reagents, 21.
 tin, list, 20.
- Groups I and II** of bases, 73, 74.
 I and II of bases, scheme, 74.
 III and IV of bases, scheme, 100, 101, 102.
 III and IV of bases, scheme when phosphates and oxalates are present, 277.
 III and IV of bases, table of preliminary work, 82.
 I to IV of bases, 165, 166.
 I to IV of bases, scheme, 166.
 I to V of bases, 218, 219.
 I to V of bases, scheme, 219.
 I to VI of bases, 259, 260.
 I to VI of bases, scheme, 260.

H

- Halides** of silver, removal, 380.
Heating in bulb tube, 335.
 on charcoal, 336, 337.
Hydriodic acid, reactions, 296.
 acid, test, 318.
Hydrobromic acid, reactions, 296.
 acid, test, 317.
Hydrochloric acid, action with silicates, 356.
 acid, insolubility of salts soluble in water in, 221.
 acid, reactions, 296.
 acid, test, 316.
 acid, treatment of salts with, 355 to 357.
Hydrocyanic acid a safer test, 320.
 acid, reactions, 296.
 acid, test, 319.
Hydroferricyanic acid, reactions, 296.
 acid, test, 322.
Hydroferrocyanic acid, reactions, 296.
 acid, test, 321.
Hydrofluoric acid, reactions, 296.
 acid, test, 311.
 acid, treatment of insolubles with, 386.

- Hydrogen**, safety tube test for, 252.
 sulphide, action on a ferric solution, 82.
 sulphide, decomposed by nitric acid, 222.
 sulphide, generator, 409.
 sulphide, reactions, 296.
 sulphide, test, 121, 323.
Hydrosulphuric acid, reactions, 296.
 acid, test, 323.

I

- Individual reagents**, 408.
 reagents, list, 7.
Insolubility in hydrochloric acid of salts soluble in water, 221.
 in nitric acid of salts soluble in water, 359.
Insoluble substances, list, 374.
Insolubles, boiling with sodium hydrate, 376.
 decomposed by sodium carbonate, 383.
 fusion with acid potassium sulphate, 387.
 fusion with sodium carbonate, 381, 382.
 treatment with hydrofluoric acid, 386.
Introduction to salt analysis, 331.
Iron, ferrous and ferric, 83.
 Group, list, 18.
 hydrate, properties, 82.
 reactions, 82.
 sulphide, properties, 82.
 tests, 86, 87, 88.
Isolation of elements not necessary, 23.

K

- Knowledge** of conditions, 3, 4, 37.
Known solution, examination of, 22.
 solution, Group I, 27.
 solution, Group II, 46.
 solution, Groups III and IV, 99.
 solution, Group V, 178.
 solution, Group VI, 237.

L

- Laboratory notes** on unknown solutions, 71.
 work in Qualitative Analysis, division of, 392.
Laws of Berthollet, 6.

(References are to sections.)

Lead chloride, properties, 172.
found in two places, 190.
hydrate, properties, 172.
reactions, 172.
sulphate, removal, 379.
sulphide, orange-red, 194.
sulphide, properties, 172.
trace in filtrate from Group V, 224.
trace in filtrate from Groups V and VI, 265.

Lithium, flame test, 25.

Litmus, early use, 2.

M

Magnesium

ammonium arsenate, 249.
ammonium phosphate, 62.
carbonate, properties, 38.
delicate test, 62.
phosphate, properties, 38.
reactions, 38.
removal, 78.

Manganese bead test, 129.

hydrate, properties, 82.
reactions, 82.
sulphide, properties, 82.

Mercuric amido chloride, properties, 172.

salts, 170.
sulphide, properties, 172.

Mercurous chloride, properties, 172.
salts, 170.

Mercury chloride, properties, 172.

confirmatory test, 195.
exists in two states, 170.
reactions, 172.
sulphide, properties, 172.

Metals, 12.

action with acids, 359 to 361.
rare, 14.

Mirror, antimony, 253.

arsenic, 253.

N

Nascent chlorine, 117, 197, 244, 246.

Natural silicates, analysis, 385.

Nickel hydrate, properties, 82.

reactions, 82, 100, 115, 116, 117, 118.
sulphide, properties, 82.
trace in filtrate from Groups III and IV, 169.

Nitric acid, action on alloys, 359 to 361.

acid, action on metals, 359 to 361.
acid, decomposed by hydrogen sulphide, 222.

acid, insolubility of salts soluble in water in, 359.

acid, reactions, 296.

acid, test, 324.

acid, treatment of salts with, 358 to 361.

Notebook, 11, 99.

sample page, 72, 390.

Notes on scheme for Group I of bases, 28 to 34.

on scheme for Group II of bases, 48 to 62.

on scheme for Group V of bases, 180 to 204.

on scheme for Group VI of bases, 239 to 253.

on scheme for Groups I and II of bases, 75 to 79.

on scheme for Groups III and IV of bases, 103 to 140.

on scheme for Groups III and IV of bases in presence of phosphates and oxalates, 278 to 287.

on scheme for Groups I to IV of bases, 167 to 169.

on scheme for Groups I to V of bases, 220 to 226.

on scheme for Groups I to VI of bases, 261 to 271.

on scheme for preliminary analysis of salts, 341 to 347.

use, 48, 99, 103.

O

Organic acids, 288.

Oxalates, effect on Groups III and IV of bases, 271, 272 to 276.

Oxalic acid, reactions, 296.

acid, test, 310.

Oxidation of ferrous iron, 85.

of sulphides, 110.

P

Partial solution of salts, 353.

Phosphates, effect on Groups III and IV of bases, 271, 272 to 276.

Phosphoric acid, reactions, 296.

acid, test, 308.

Plaited filter, 109.

Plant juices, use, 2.

(References are to sections.)

Platinum, 14.
 foil, 129.
 foil, use, 352.
 test wire, how to clean, 25, 34.
Potassium carbonate, use as a flux, 382.
 flame test, 25.
 nitrate, use in fluxes, 382.
 reactions, 25, 32, 33.
 sulphate, acid, use as a flux, 387.
 wet test, 33.
Precipitate, dissolving on the filter paper, 53.
 oxidation of, 110.
 washing the, 111.
Precipitated sulphur in filtrate from Groups III and IV, 169.
Preliminary analysis of salts, 333.
 analysis of salts, scheme, 334 to 340.
 work for acids, 292 to 296.
 work for acids, reagents for, 421.
 work for bases, reagents for, 410.
 work for Group I of bases, 25, 26.
 work for Group II of bases, 36, 38.
 work for Groups III and IV of bases, 81, 82.
 work for Group V of bases, 171, 172.
 work for Group VI of bases, 228, 229.
Preparation of the solution of salts, 348.
Prevention of bumping, 121.
Properties of salts, general, 334.
Prussian blue, 87.

Q

Qualitative Analysis, definition, 1.
 division of work in, 392.
Questions for study, 394 to 406.

R

Rare metals, 14.
Reaction, definition, 5.
 in the dry way, 5.
 in the wet way, 5.
Reading, collateral, 391.
Reagent, definition, 5.
 general, definition, 5.
 special, definition, 5.
Reagents, complete list, 407.
 for preliminary work for acids, 421.
 for preliminary work for bases, 410.

for unknown solutions, 410.
 general, 409.
 group, 21.
 individual, 408.
 list of individual, 7.
Reduction of ferric iron, 84.
Removal of bases by hydrogen sulphide, 370.
 of bases by sodium carbonate, 368, 369.
 of carbon, 378.
 of lead sulphate, 379.
 of silver halides, 380.
 of sulphur, 378.
Requirements for successful work, 3.

S

Safety tube test for hydrogen, 252.
Salt Analysis, 331 to 390.
 analysis, introduction, 331.
Salts, 12.
 action with sulphuric acid, 340.
 general properties, 334.
 giving acid solution, 350.
 giving alkaline solution, 350.
 preliminary analysis, 333.
 preparation of the solution, 348.
 scheme for preliminary analysis, 334 to 340.
 scheme for the preparation of the solution of, 364.
 treatment with acids, 354.
 treatment with aqua regia, 362.
 treatment with hydrochloric acid, 355 to 357.
 treatment with nitric acid, 358 to 361.
 treatment with water, 349.
Sample page from laboratory notebook, 72, 390.
Scheme for acid analysis, 327 to 330.
 for Group I of acids, 328.
 for Group I of bases, 27.
 for Group II of acids, 329.
 for Group II of bases, 47.
 for Group III of acids, 330.
 for Group V of bases, 179.
 for Group VI of bases, 238.
 for Groups I and II of bases, 74.
 for Groups III and IV of bases, 100, 101, 102.
 for Groups III and IV of bases in presence of phosphates and oxalates, 277.

(References are to sections.)

for Groups I to IV of bases, 166.
 for Groups I to V of bases, 219.
 for Groups I to VI of bases, 260.
 for preliminary analysis of salts,
 334 to 340.
 for preparation of solution of
 salts, 364.
Secondary reactions, 407.
Shaking a precipitate, 184.
Short cuts, 140.
Silica, absorbed from glass by sodium
 hydrate, 124.
 action with hydrofluoric acid, 386.
Silicates, action with hydrochloric
 acid, 356.
 analysis of natural, 385.
Silicic acid, reactions, 296.
 acid, test, 314.
Silver chloride, properties, 172.
 halides, decomposition of, 380.
 halides, removal, 380.
 nitrate group of acids, 290.
 oxide, properties, 172.
 reactions, 172.
 sulphide, properties, 172.
Sodium carbonate, a flux for insol-
 ubles, 381, 382.
 flame test, 25.
 hydrate, spoils on standing, 124.
 nearly always present, 29.
 reactions, 25, 29, 30.
Solubilities, Table of, 371, 372.
Solution, known, examination of, 22.
 of salts, scheme for preparation,
 364.
 unknown, examination of, 22.
Special reagent, definition, 5.
 tests before fusion, 377.
 tests for acids, 301.
Stannic sulphide, properties, 229.
Stannous chloride, reagent, 198.
 sulphide, properties, 229.
Stirring rod, 11.
Strontium carbonate, properties, 38.
 flame test, 38.
 oxalate, properties, 38.
 phosphate, properties, 38.
 reactions, 38.
 sulphate, properties, 38.
Study, course of, 12.
 Questions, 394 to 406.
Substances, insoluble in water or
 acids, treatment of, 373.
Suggestions to the teacher, 422.
Sulphides, oxidation of, 110.

Sulphur, removal, 378.
Sulphuric acid, action of salts with,
 340.
 acid, expulsion, 199.
 acid, reactions, 296.
 acid, test, 315.
Sulphurous acid, reactions, 296.
 acid, test, 306.

T

Table of preliminary work for acids,
 296.
 of preliminary work for Group II
 of bases, 38.
 of preliminary work for Group V of
 bases, 172.
 of preliminary work for Group VI
 of bases, 229.
 of preliminary work for Groups III
 and IV of bases, 82.
 of solubilities, 371, 372.
Tartaric acid, reactions, 296.
 acid, test, 312.
Teacher, suggestions to the, 422.
Terms frequently used, 5.
Test
 blank, 32, 327.
 for ammonium, 26.
 for hydrogen sulphide, 121, 323.
 wire, when not in use, 34.
 wire, how to clean, 25, 34.
Tests for iron, 86, 87, 88.
Thiosulphuric acid, reactions, 296.
 acid, test, 307.
Tin, exists in two states, 227.
 Group, list, 20.
 reactions, 229.
 sulphide, colloidal, 241.
 sulphides, properties, 229.
 trace in filtrate from Groups V and
 VI, 265.
Traces, 407.
**Treatment of insolubles with hydro-
 fluoric acid**, 386.
 of salts with acids, 354.
 of salts with aqua regia, 362.
 of salts with hydrochloric acid,
 355 to 357.
 of salts with nitric acid, 358 to
 361.
 of salts with water, 349.
 of substances insoluble in water
 and acids, 373.
Turnbull's blue, 87.

(References are to sections.)

U

Unknown, solution, examination of, 22.
solutions, reagents for, 410.
Uranium, 14.
Use of notes, 48, 99, 103.

W

Wash bottle, 11.
Washing the precipitate, 111.

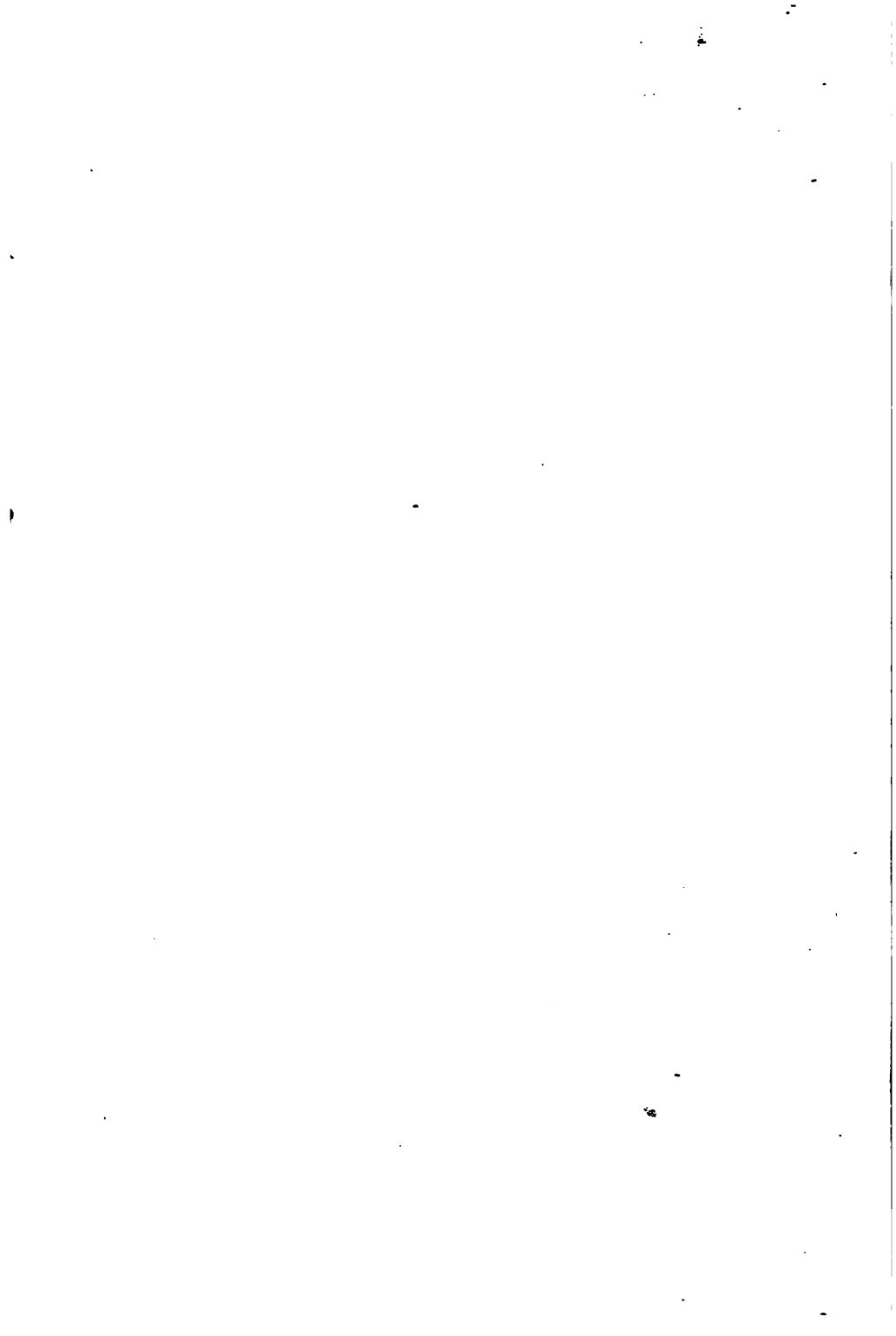
Wet test for potassium, 33.
way, reaction in the, 5.

Y

Yellow ammonium sulphide, reagent, 268.

Z

Zinc hydrate, properties, 82.
reactions, 82.
sulphide, properties, 82.
sulphide, how distinguished from sulphur, 131.



~~Taken;~~

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